ISOTOPIC TRACERS IN CATALYTIC MECHANICAL STUDIES

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I thought it was important to give a sampling of the wide variety of ways that tracers are used, but the variety is so great that I can't do justice to any one of these. Instead, I'm going to indicate some different approaches. The previous speakers have focused their attention on the catalyst surface, either on a single crystal, or in the form of a commercial catalyst, and have shown how the chemical-physics approaches, the tools available, can provide much useful information. I'm going to take a look at the gas phase and show that tracers can tell about the intermediates that must be formed in reactions or the nature of the adsorbed species or the quantity thereof. One of the chief uses of tracers is in determination of mechanisms, that is in the interpretation of kinetics. Industry has been very adept at developing new catalysts based on kinetic studies; but for future improvement we need to know what's going on in a reactor. When industry uses a catalyst, it has certain objectives and tolerances to meet. Often this can be achieved with very little idea what's going on inside the reactor. But, when these processes must run for a long time and when operational difficulties arise, knowledge of mechanism is exceedingly important.

The first slide points out the great sensitivity that radio carbon gives in measuring very small adsorptions. This is taken from work of McIver and Emmett using a radioactive hydrocarbon adsorbed on a silica alumina surface. The question was, is there any chemisorption. This couldn't be measured by straight forward volumetric techniques but can with radiocarbon. Here the amount of chemisorption is plotted as a function of gas volume. One could very easily get at least three orders of magnitude more sensitivity so that one could measure the adsorption on as little as a square centimeter of surface, if one really wanted to do this, using radio isotope dilution technique.

This slide deals with the Fisher-Tropsch process. From product distribution data available in the early 50's, Fischer-Tropsch appeared to involve carbon chain growth by the addition of one carbon at a time. Kummer and Emmett saw that if they were able to add a radioactive compound that would initiate the chain, the resultant product molecules should all have the same molar radioactivity. This was very nicely confirmed when radioactive ethanol was added. This is just one type of tracer experiment where one adds something that's radioactive and sees what happens to it in the products.

The next slide shows the mechanism that was deduced. In the growing chain a C_1 group adds to a C_N by one of two simple condensation reactions, and there are two ways to split out water. One way will lengthen the chain by one carbon atom, one will form a methyl group thus explaining the unusual product distribution one finds in the Fisher-Tropsch synthesis. My personal opinion is that we'll be very interested in this synthesis again to make fuels from coal.

This slide is taken from the work of Van Hook and Emmett. It illustrates a very interesting point. In the cracking of cetane or other paraffins it is widely thought that the mechanism is one of simply breaking down the cetane molecule in a way described by Greenfelder. By adding a little radioactive propylene these workers were able to show that radioactivity was distributed particularly in the C_8-C_9 range, even into the aromatics that are formed, and that catalytic cracking involves the reverse steps as well.

This slide lists mechanisms which had been suggested in the literature for the isomerization of the n-butenes. The point here is that these mechanisms except the top one suggest that one molecule isomerizes to a second one, and a second one goes to a third one. By employing radio carbon techniques, we were able to show which mechanism was operative over a Silica-Alumina catalyst. If the first reaction applies, as for example through the formation of a common intermediate carbonium ion then the initial product formed in this first order reaction is going to reflect the zero activity of the one-butene and so will have zero activity. On the other hand, if the second path dominates, then at all stages of the reaction the trans-2-butene forming will have the same radioactivity as existing in the cis-fraction so that the value of alpha, which is the radio activity of the trans-product divided by the radioactivity of the cis-2-butene, is always unity.

And on the next slide, we see that reality conforms very nicely to this mechanism and extrapolates to zero; whereas, for the second mechanism, the predictions are widely variant from the experimental results. The point is that tracers can very frequently be used to distinguish between different suggested mechanisms.

The next slide shows data for the deuterium that is incorporated in ethane when ethylene is hydrogenated over metal surfaces. Up until the '50's it was thought that hydrogenation of ethylene with D_2 should yield 1-2-dideutero ethane. In fact, it does but there is produced still more d_1 and d_o than d_2 ethanes and this leads to the concept of the half hydrogenated state where deuterated ethyl groups are formed reversibly. Hence, both exchanged ethylenes and ethanes are produced in this sort of distribution. You see how well it fits for a wide variety of different catalyst systems.

The next slide illustrates another general technique developed by Kemball and used widely by Kemball and Burwell in the study of the intermediates that may form on different surfaces. The idea here is to take a molecule which will exchange with deuterium but not react otherwise on the surface and determine the deuterium distribution in the products. This is expressed as a summation in ϕ which can be calculated for equilibrium. Experiment always produces first order plots of log $(\phi_\infty - \phi)$ versus time and the slope of this line gives a rate constant k_∞ for the exchange process. From the same data one can calculate the rate of disappearance of the d_o leading to a rate constant k_o and the ratio of these constants is a parameter, M, which shows whether one hydrogen or more exchanges with deuterium per residence on the catalyst surface. These data are the work of Hightower and myself in which the exchange was carried out between the hydrogens of cyclopentene and D_2 over an alumina surface.

And rather interestingly, only two out of the total of eight hydrogens in the molecule exchanged with d_2. The plots show that these two exchanged one at a time. Now that raises an interesting point which I'll take up in a moment.

Another way one can use tracers is to examine the products by high resolution NMR. The next slide shows the spectrum of the undeuterated molecule compared with the spectrum of the partially deuterated molecule; the spectra are virtually identicle except in the region at the left where there is a vast difference which corresponds to the exchange of the two vinyl hydrogens. The reaction is quantitative. The fact that only the two vinyl hydrogens exchange and not the rest is both interesting and important. This means that the hydrogens here must be replaced either in a concerted reaction or by removal of the hydrogen from the hydrocarbon before a deuterium is added. If the deuterium were added first, then the exchange would walk around the molecule leading to exchange at all positions. This doesn't happen and so evidently rupture of the carbon-hydrogen bond is an important part of the reaction mechanism. And the next slide shows that this is confirmed by the isotope effect measurements. This large value of the isotope effect derived from the exchange of a cyclopentene plus D_2 as compared with the exchange of cyclopentene D_2 with hydrogen. Isotope effects are not always easy to interpret. But when they are this large it certainly is indicative that rupture of the carbon-hydrogen bond is important in the rate determining step and that fits our other data.

The next slide is a whole talk in itself but I wanted to indicate that Herman Pines used to make the very good point that a molecule that can act as a model compound can give information that can be obtained in no other way. Here is such a compound that we've used, namely the erythro-2-butanol-3d, in the study of alcohol dehydration. If the erythro molecule yields cis-D-1 and trans-D-0, the implication is that the reaction goes by anti-elimination, by removal of OH and the d from the opposite side of the molecule, whereas if it yields cis-D-o and trans-D-1 this means there is syn-elimination with removal from the same side of the molecule. We confirmed Herman's point that over alumina there is anti-elimination, as he found with the methyl-cyclo-hexanols, but over more acidic, Bronsted-type catalyst, there is syn-elimination, demonstrating a significant difference in the type of mechanism, depending on the type of surface involved. That this selectivity occurs at all shows that this is not a carbonium mechanism because in that case stereo-selectivity would be lost.

The reaction of the oxidation of ethylene over silver-type catalysts is unique in that it is the only catalyst that produces ethylene oxide, and is the only partial oxidation product that's formed. This slide shows some work of Parravano where he exchanged radioactive ethylene with ordinary oxide and found that the radioactivity was transfered to the ethylene oxide and was lost from the ethylene fraction, suggesting that the reactions went by picking up an oxygen from some place on the surface to form the ethylene oxide, and the reverse reaction was also maintained. There has been a big debate in literature about whether ethylene oxide is formed from an adsorbed 0_2 or an 0_1 species. Whereas this work doesn't prove it, it certainly suggested that it's an O_1 species that is involved in the reaction.

Shown on the next slide are the spectra of the ethylene oxides obtained from 1-1 dideuteroethylene, cis and trans-dideuteroethylene oxides. Briefly, regardless whether you start with cis 1-2 dideutero-ethylene or trans, the same ethylene oxide product is obtained. This is nearly equi-molar mixture of the two species. The work with the 1-1 dideutero ethylene shows that no intra- nor inter-molecular exchange occurs so that in the course of forming ethylene oxide the double bond opens letting the CH_2 groups rotate relative to each other.

The next slide shows that over silver, whether the per-deutero-olefin or the ordinary ethylene is oxidized, a very large inverse isotope effect occurs, too large to be accounted for in any ordinary way. Inverse isotope effects are usually very small.

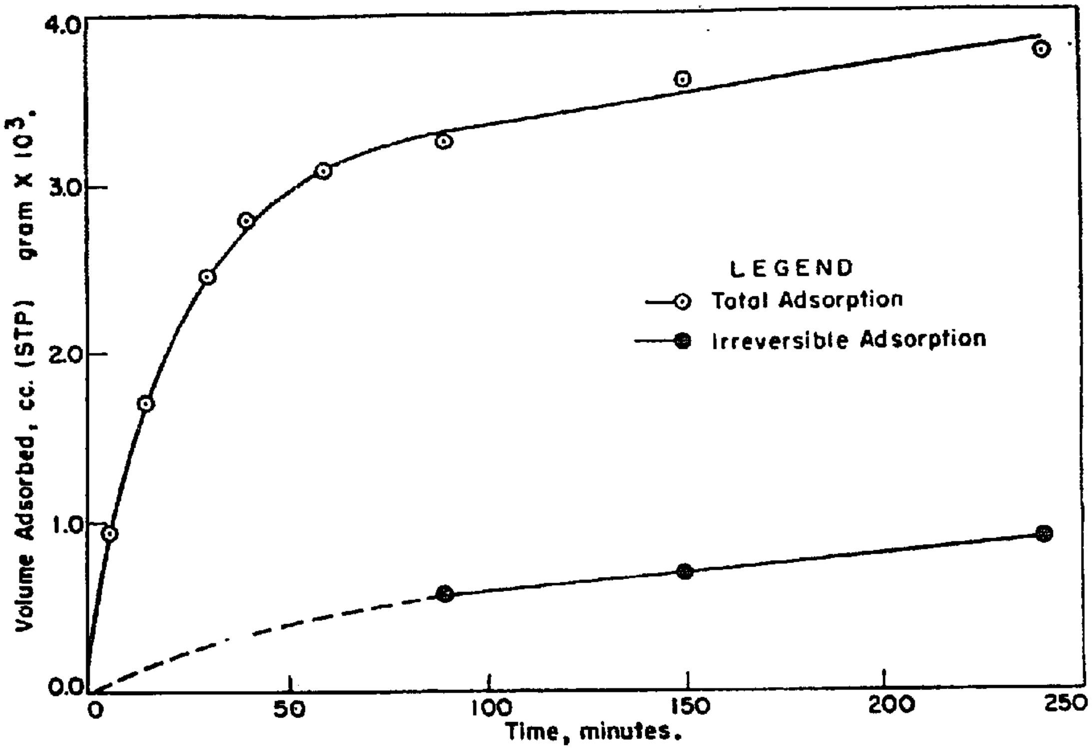
The next slide suggests the olefin forms an intermediate on the surface (not necessarily the one shown) before changing to the eipoxide. Carbon hydrogen bonds are not broken in this step but they are on the path to total oxidation and it is here that we expect the isotope effect. The steady state treatment on this intermediate shows that the inversion arises naturally. Hence, the inverse isotope effect occurs because it's harder for the intermediate to undergo total oxidization in the case of the perdeutero-compound.

The next slide summarizes some findings of oxidation catalysis over the noble metals. In the oxidation of ethylene over palladium or iridium, the methyl group is formed by an intra-molecular shift of a hydrogen from one carbon to the other. This was established by oxidizing an equimolar mixture of ordinary and perdeutero-ethylene; the methyl groups formed were both CH_3 and CH_2D. Rhodium, ruthenium and gold all oxidize propylene, going through a symmetrical intermediate of the type described by Adams and Jennings for reaction to acrolein. Iridium is found to cleave the double bond specifically. This convinced us that these catalysts cannot be assumed to behave more or less alike. This was important when the problem of finding an NO_x catalyst came up. It was suggested that platinum need not be representative of platinum group metals. Thus, the unique ruthenium catalyst system was discovered by Drs. Kobolinsky and Taylor at Gulf.

The last slide is taken from the work of Keulks in which oxygen 18 was used in the oxidation of propylene over a bismuth molybdate catalyst. The catalyst initially contained no oxygen 18. You note that all the products except the propylene oxide are very low in oxygen 18 compared with the gas phase and the propylene oxide is thought to form by a homogeneous gas phase reaction which was not operative for the surface catalyst reactions. This data together with mass balance data indicate that during the oxidation of propylene over bismuth-molybdate the whole mass of the oxide becomes labile and takes part in the reaction. This is a hurried thumbnail sketch of some of the uses of tracers and I'm sorry I didn't have time to go into details.

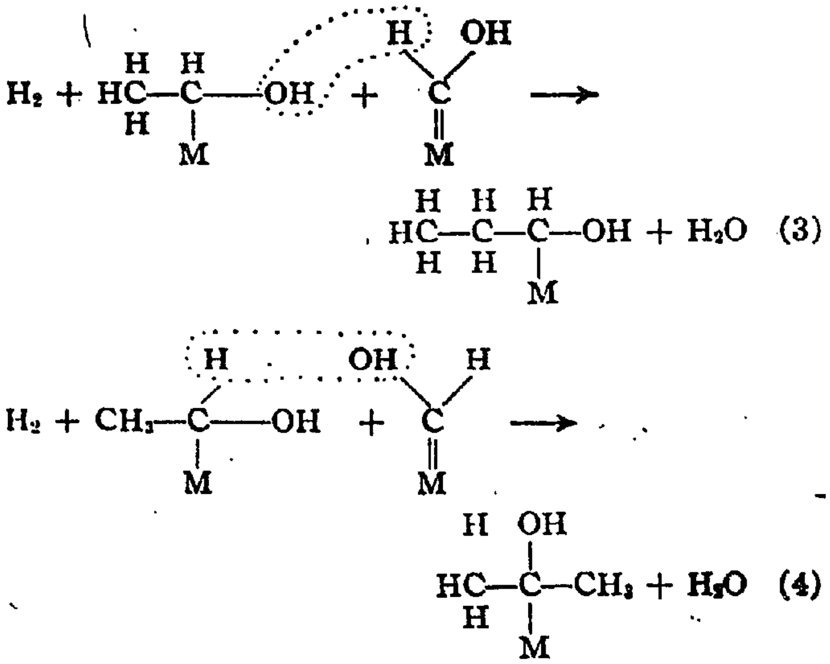
Hightower: Many other tracers can be used, such as C^{13}, N^{15}, S^{34}, C^{14}, regardless how complex is the reaction to be investigated.

286



Rate of chemisorption of isobutane-2-C^{14} on silica-alumina at 150° and 10 mm.

1



Suggested Mechanism of
Fischer-Tropsch Synthesis
by J. T. Kummer and P. H. Emmett
J. Am. Chem. Soc., 75, 5177 (1953).

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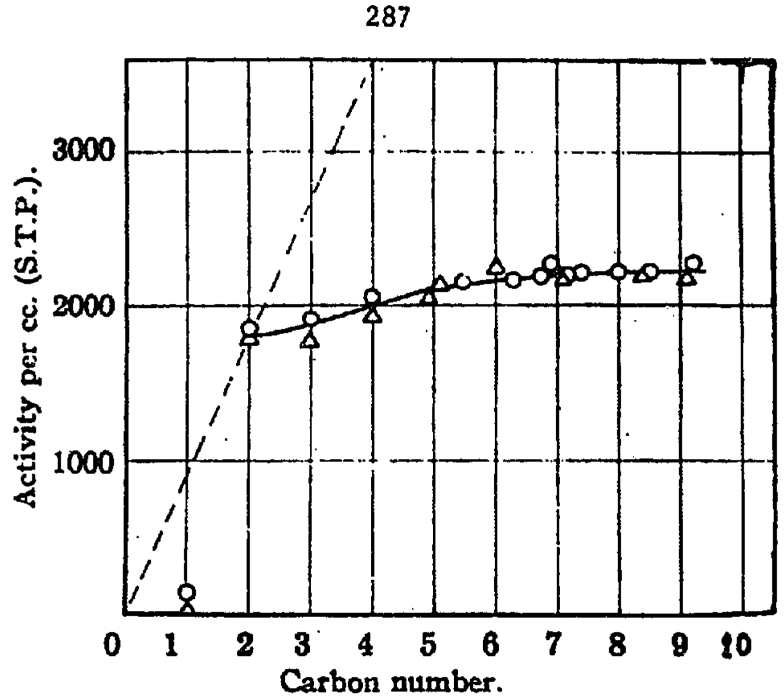
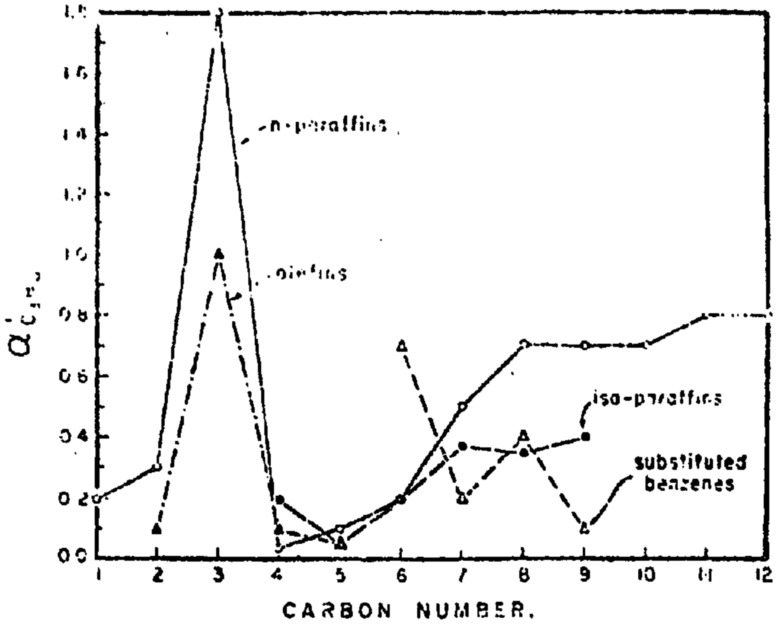


Radioactivity of Products when $Ch_3C^{14}H_2$ OH was added to Fischer-Tropsch Systhesis by J. T. Kummer, H. H. Podgurski, W. B. Spencer and P. H. Emmett - J. Am. Chem. Soc., 73, 564 (1951).



Incorporation of C_3H_6-1-^{14}C into Products during Cetane Cracking - W. A. van Hook and P. H. Emmett, J. Am. Chem. Soc., 84, 4410 (1962)

POSTULATED MECHANISMS FOR BUTENE ISOMERIZATION

1) Classical sec-Butylcarbonium Ion Intermediate

$$\begin{tikzcd}
\text{1-Butene} \arrow[rr, shift left] \arrow[dr, shift left] & & \text{cis-2-Butene} \arrow[ll, shift left] \arrow[dl, shift left] \\
& \text{trans-2-Butene} \arrow[ul, shift left] \arrow[ur, shift left] &
\end{tikzcd}$$

(Products formed in equilibrium ratios)

2) Two Separate Reactions: Double Bond Shift and cis-trans Isomerization, e.g.,

$$\text{1-Butene} \rightleftharpoons \text{cis-2-Butene} \rightleftharpoons \text{trans-2-Butene}$$

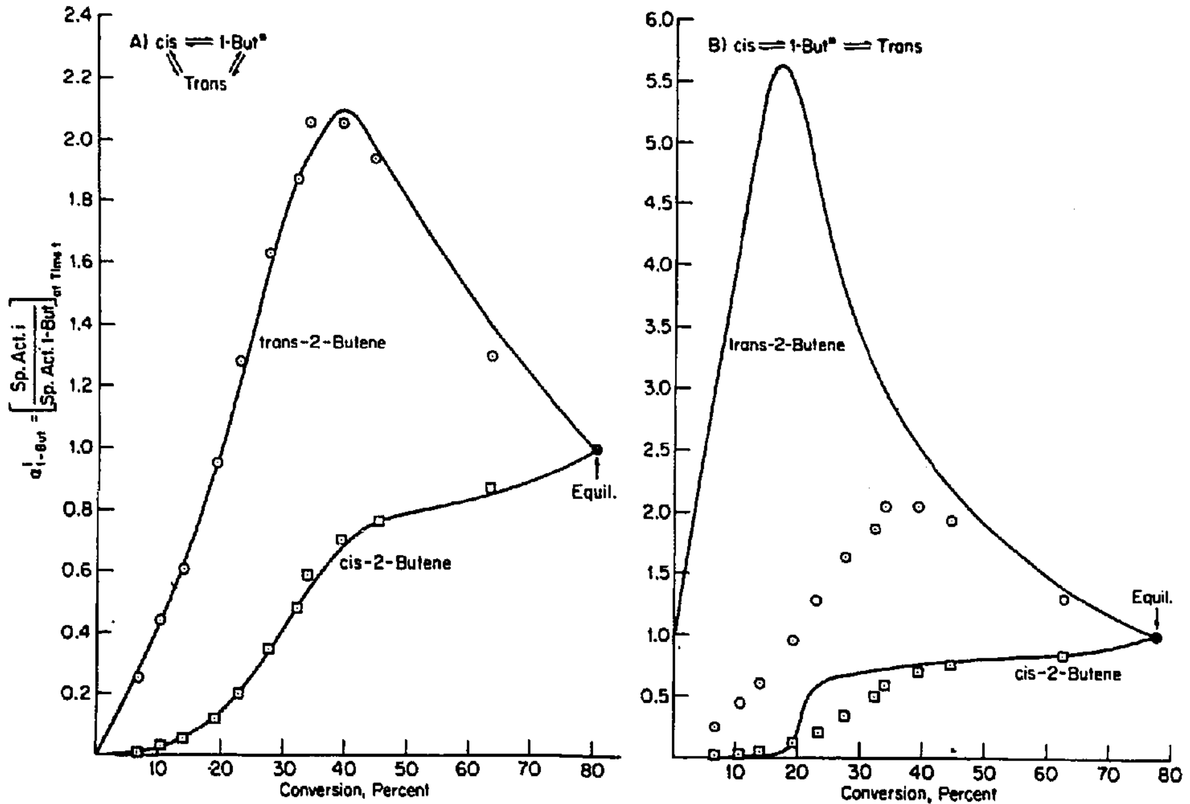
3) Allylic Carbonium Ion:

$$\text{cis-2-Butene} \underset{+H^-}{\overset{-H^-}{\rightleftharpoons}} \text{cis-CH}_3\text{-}\underset{\oplus}{\underline{\text{CH-CH-CH}_2}} \underset{-H^-}{\overset{+H^-}{\rightleftharpoons}} \text{1-Butene}$$

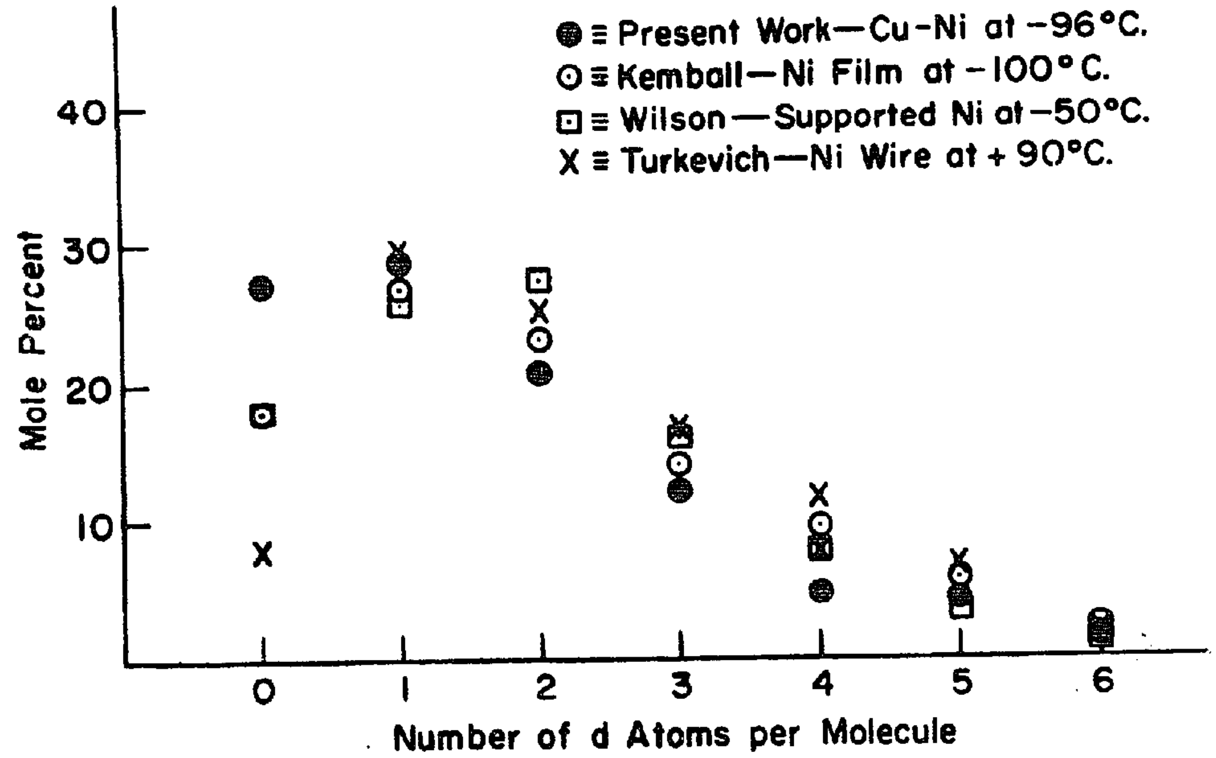
$$\text{1-Butene} \underset{+H^-}{\overset{-H^-}{\rightleftharpoons}} \text{trans-CH}_3\text{-}\underset{\oplus}{\underline{\text{CH-CH-CH}_2}} \underset{-H^-}{\overset{+H^-}{\rightleftharpoons}} \text{trans-2-Butene}$$

4) Hydrogen-Switch Mechanism:

$$\text{cis-2-Butene} \rightleftharpoons \text{1-Butene} \rightleftharpoons \text{trans-2-Butene}$$



a-Value Plot for Products of cis-2-Butene (1-Butene, C^{14}) Isomerization over Synthetic Silica-Alumina, DSA-1, at 23°. Points are Experimental; Calculated Lines Based on Two Models.



Distribution of Deuterium in Ethane

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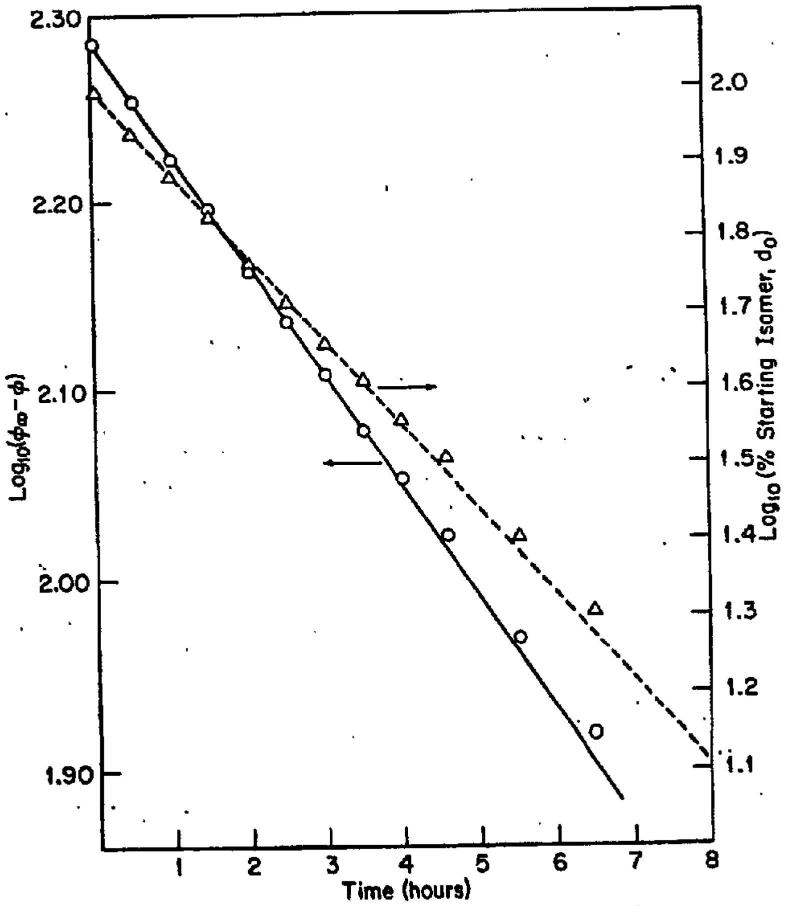


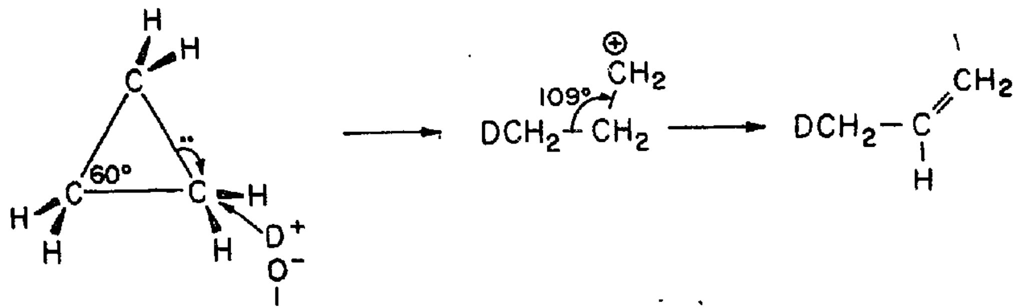
Exchange of two vinyl hydrogen atoms in cyclopentene with D_2 at 18°C.

8

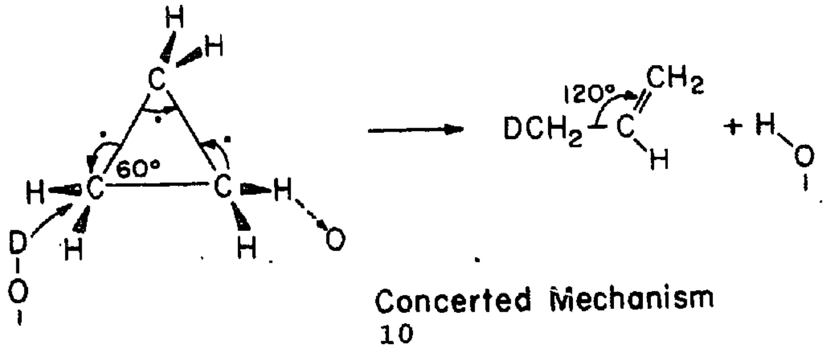
ACTIVATION ENERGIES AND ISOTOPE EFFECTS OVER ALUMINA

Reaction	Activation Energy kcal/mol	Isotope Effect k_H/k_D
Cyclopentene + D_2 vs. Cyclopentene-d_2 + H_2	5.9	2.8
CH_4 + D_2 vs. CD_4 + H_2	5.7	1.8
1-Butene → 2-Butenes	13	3.5
Effect of Catalyst OH/OD	-	1.0

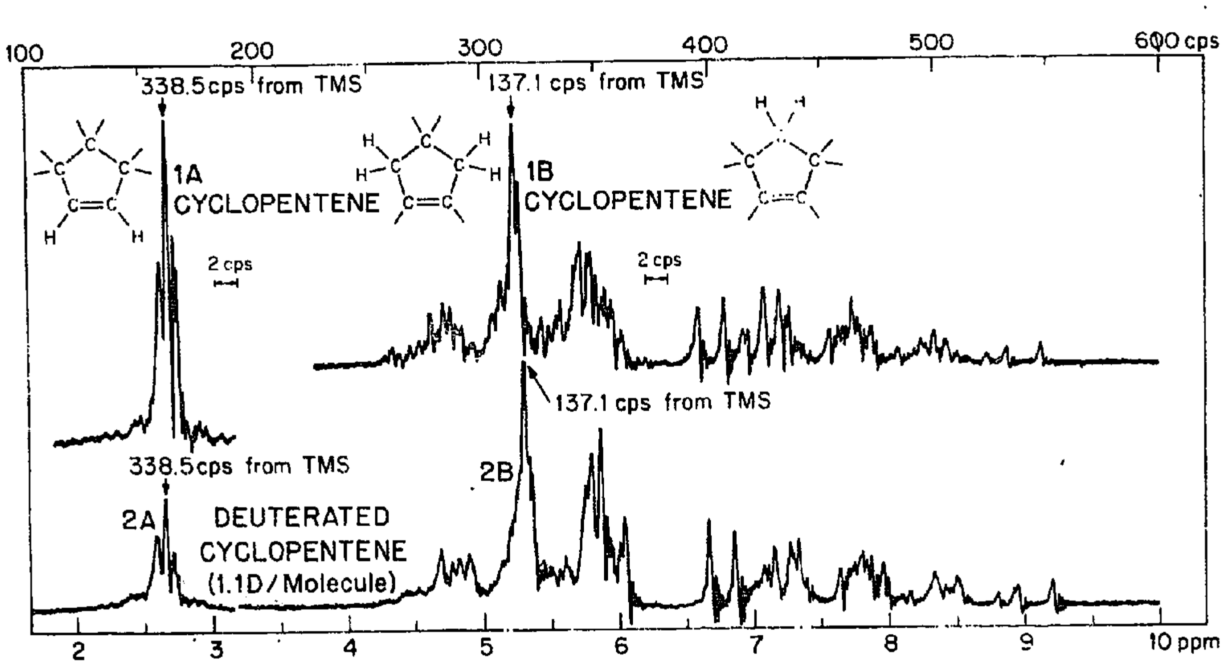
POSSIBLE MECHANISMS OF CATALYTIC ISOMERIZATION OF CYCLOPROPANE



Roberts Mechanism
J. Phys. Chem. 63, 1400 (1959)



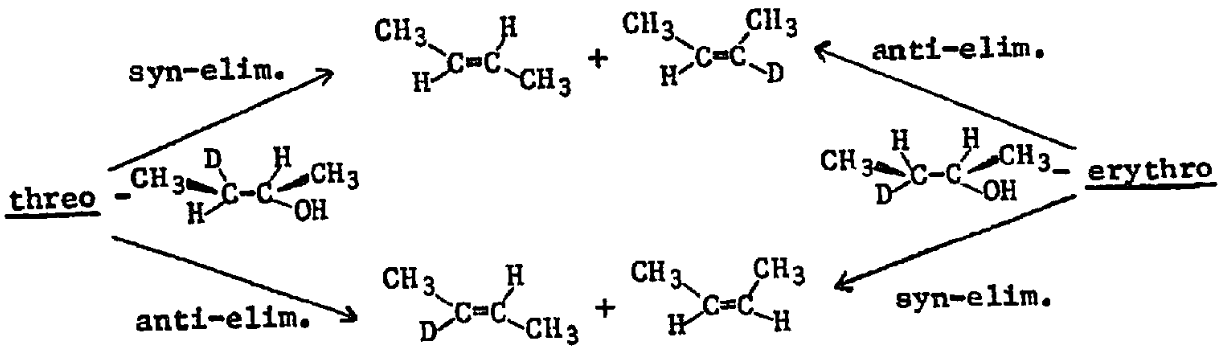
Concerted Mechanism



NMR Spectra of Identical Samples of Cyclopentene and Partially Deuterium-Exchange Cyclopentene Dissolved in CCl_4-TMS Solution.

11

Olefin Forming Elimination Reactions of Threo- and Erythro-2-Butanol,3d_1



12

OXYGEN TRANSFER CATALYZED BY Ag AND Au

$$^*C_2H_4 + C_2H_4O \underset{k'}{\overset{k}{\rightleftharpoons}} C_2H_4 + {}^*C_2H_4O$$

or

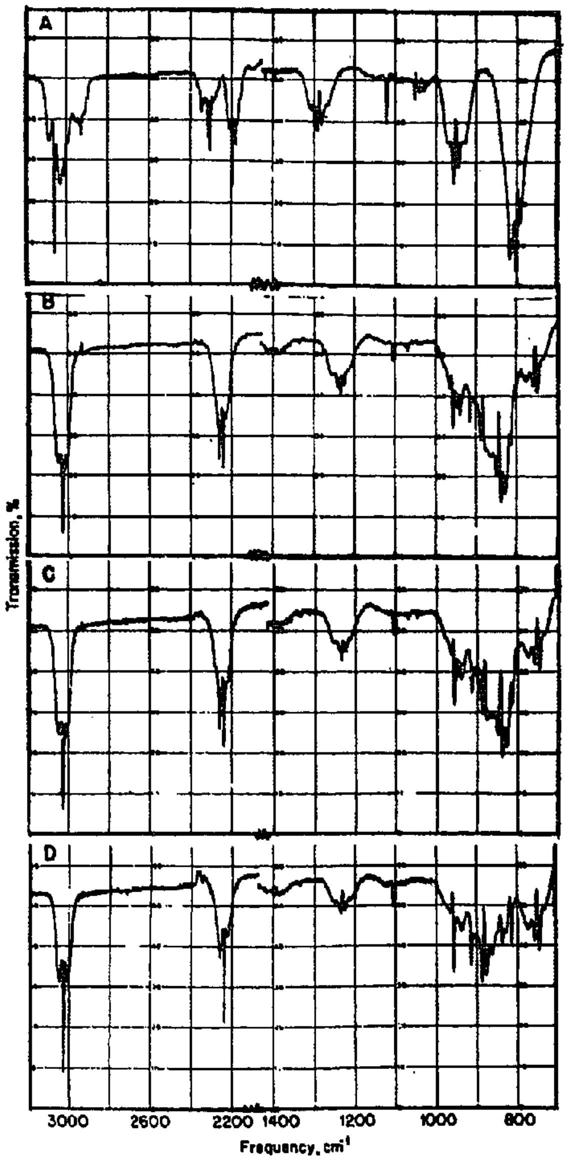
$$^*C_2H_4 + O(s) \xrightarrow{k} {}^*C_2H_4O \qquad \text{and}$$

$$C_2H_4O \xrightarrow{k} C_2H_4 + O(s)$$

1) $k \doteq k_\circ (P_{ETO}/P_{ET})^m \quad (1 < m < 0.5)$

2) k (Au at 177°) = 6×10^{-8} mol.m^{-2}sec^{-1}atm^{-1}
   k (Ag at 174°) = 1×10^{-10} " " " "

*G. Manara and G. Parravano, *J. Catalysis*, *23*, 379 (1971).



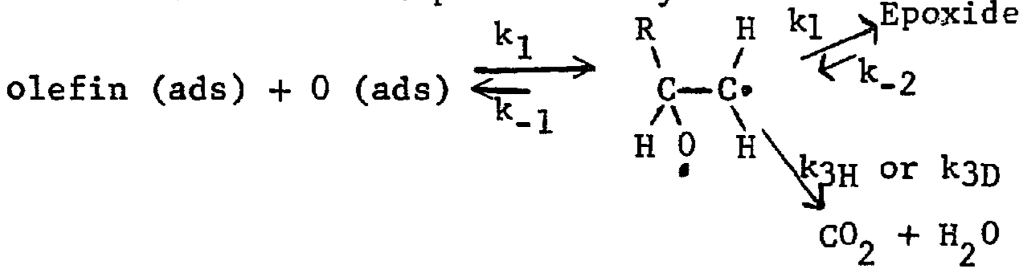
Infrared Spectra of Dideutero Ethylene Oxides prepared from: A, gem-$C_2H_2D_2$ over Ag; B, cis-$C_2H_2D_2$ over Ag; C, trans-$C_2H_2D_2$ over Ag; D, trans-$C_2H_2D_2$ via Bromohydrin.

ISOTOPE EFFECTS IN EPOXIDATION OVER Ag AT 165°C

Olefin	Oxid. Rate, μM/min to $CO_2 + H_2O$	Oxid. Rate, μM/min to Epoxide	Selectivity, %	Isotope Effect, k_D/k_H to CO_2	Isotope Effect, k_D/k_H to Epoxide
C_2H_4	3.4	3.0	46	-	-
C_2D_4	2.7	5.6	67	0.8	2.0
C_3H_6	5.3	0.14	2.7	-	-
C_3D_6	4.2	0.38	8.3	0.8	2.6
CD_3CHCH_2	4.0	0.43	9.8	0.9	3.5
CH_3CHCD_2	4.8	0.11	2.3	1.0	0.9
CH_3CDCH_2	4.0	0.13	3.0	0.7	1.0

EXPLANATION OF INVERSE ISOTOPE EFFECTS IN OLEFIN OXIDATION OVER Ag CATALYSTS

1) If the reaction is represented by



2) A zeroth approximation steady state treatment yields

$$k_D/k_H \text{ (Epoxide)} = \frac{k_2 + k_{3H}}{k_2 + k_{3D}}$$

$$k_D/k_H (CO_2) = \frac{k_{3D}}{k_{3H}} \; \frac{(k_2 + k_{3H})}{(k_2 + k_{3D})}$$

3) For propylene $k_2 \ll k_3$ and for ethylene $k_2 \approx k_{3H} \approx 2k_{3D}$

Partial Oxidation Chemistry Characterized by Tracers

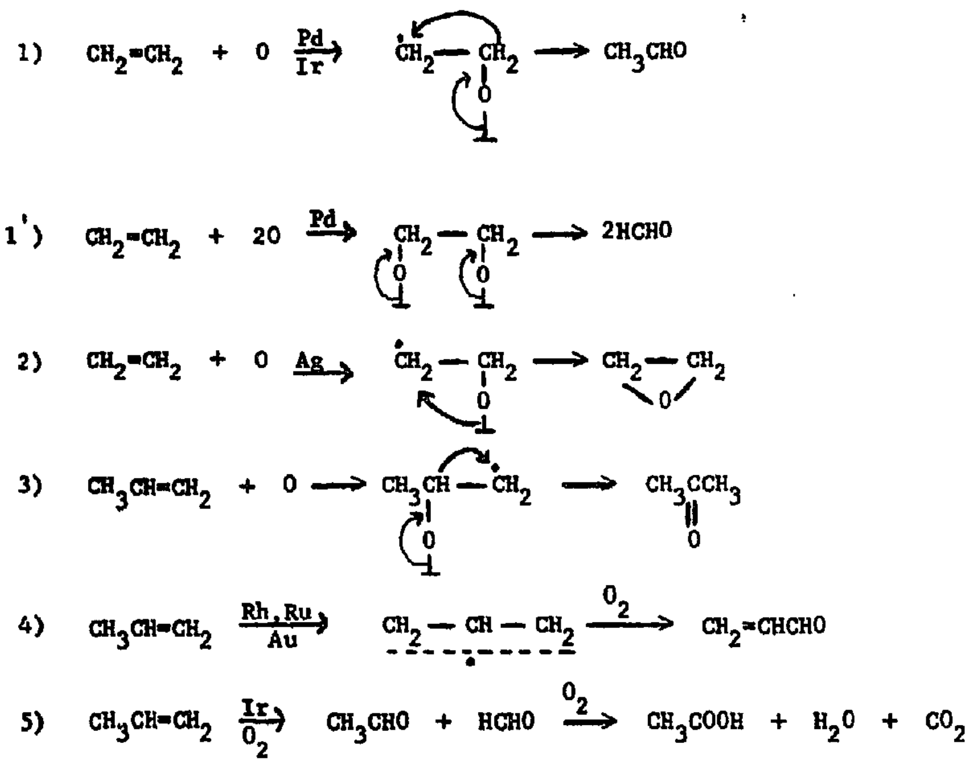


Table VIII

Results of the Oxygen-18 Studies

Products	$^{18}O/^{16}O$ Ratio					
	Bismuth Molybdate		Bismuth Molybdate Arsenate		Strontium Nitrate	Cuprous Oxide
	Reactor I	Reactor II	Reactor I	Reactor II	Reactor II	Reactor I
CO_2(46)	0.038	0.068	0.020	0.040	0.125	0.123[1]
CH_3CHO	0.020	0.070	0.025	0.040	0.130	--
Acrolein	0.043	0.066	0.030	0.085	0.095	0.085
Propylene Oxide	--	0.103	--	0.150	0.087	--
$^{18}O/^{16}O$ inlet gas	0.120	0.110	0.110	0.161	0.090	0.110

[1] Ratio of $^{18}O/^{16}O$ for CO_2 (48) was 0.007

INSIGHTS INTO THEORY OF CATALYSIS

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First of all, I want to apologize that an outsider like me is muscling in on a meeting of professionals who are faced with day to day problems in catalysis from which I must admit, I'm still remote, even though perhaps one day we will be closer to making a real impact on catalysis as such. It would be nice if I could say that I felt the time had come for solid state physics to make a contribution to surface chemistry and catalysis, but to be truthful the way I got into this was by idly paging through some Russian work a couple or three years ago, in which, I can never remember their names, Ebersuriken and Lubarsky, reported on the hydrogenation of benzene on paramagnetic nickel copper alloys as a function of the nickel concentration. And they observed that in the paramagnetic range, not on the ferromagnetic side, the activation energy hardly changed, and yet the reaction rate changed by two to three orders of magnitude as the paramagnetism of the substrate, as measured by the effective number of Bohr magnetons per atom, changed by only a factor of two or three. That made me suspicious and then I talked to Bernd Matthias and various other people at La Jolla. Bernd told me that Paravanno, as early as 1952, looking at the decomposition of formic acid over barium titanate, found

SUHL, (Continued)

that it had a little peak near the ferroelectric transition. Then I began to suspect that maybe the substrate fluctuations, which would be enhanced, charge fluctuations in the case of barium titanite and spin fluctuations in the case of the copper nickel alloys, maybe the coupling of these to the adsorbates might have something to do with these effects. Then I found out that Pataman at Batelle, Geneva, had made some experiments in which he bombards nickel with adsorbed, chemisorbed, hydrogen with electrons and watches the hydrogen ions coming off, which may be regarded as the amount of hydrogen that has survived the desorption process, and there he noticed that little peak near the ferromagnetic transition. Later on, he repeated this experiment on nickel palladium alloy, which has a lower Curie point and found that the peak moved down together with the Curie point. At the same meeting where this was reported (this was a little workshop at the University of Marseillaise last year) Heidinger, also from Batelle Geneva, reported something rather spectacular. So spectacular, that one may be skeptical, and we are repeating this experiment at La Jolla where we are the grateful recipients of an NSF grant. Heidinger reported an experiment in which he had taken a gold substrate with an aluminum oxide film and finally a thin layer of gold on top. Now, the aluminum oxide is as much as 200 or 250 Å thick, and that cast doubt on the next stage of what I am going to say. What he found was that when he ran a tunnelling current from the gold substrate to the top layer of gold, then the rate of decomposition of formic acid went up linearly with the tunnelling current. We may say, first of all, you don't get a decent tunnelling when you have a 200-250 Å layer of aluminum oxide, but probably he doesn't have a uniform layer. Then you may argue, perhaps he has pin holes and maybe there's an electrolysis effect or something else going on here. We are checking this experiment at La Jolla now. We have observed the same Heidinger effect under the same circumstances. But we are now going to try to make controlled very thin layers of oxides for a better indication of something real. It is apparently not an ordinary heating effect, because Heidinger checked that rather carefully. Now, perhaps the charge fluctuations due to the hot electrons that are tunneling to the top gold layer decay to the Fermi level and stir up whole electron pairs and maybe these are incoherent charge fluctuations which couple to the electric dipole moment of the formic acid and break it up. But this is all rather speculative in the literature. There are many pseudo-facts which are suggestive. Recently, and this is my pièce de résistance, there have been some experiments by Mickey Shanaberger at Santa Barbara. With a thin nickel film of about 1000 - 1500 Å he measured resistivity after allowing hydrogen to chemisorb on it. He found that the resistance of this film changed by between 5 and 10%, presumably due to the increased surface scattering, or due to the fact that the electron shared between the hydrogen and the nickel substrate becomes partly available for conduction. Whatever the reason, the presence of hydrogen causes an incremental increase in the resistance. So, following some experiments of George Faher at La Jolla,

SUHL (Continued)

I suggested to measure the change in the resistance as a function of time when the hydrogen comes on or off, and the change in the Johnson noise or the nonequilibrium part of the Johnson noise, evidenced by running a current through the sample. He found that the time constant was so long that he did not need to measure noise setup, and so he watched the decline of the increment of increase in resistance to zero as the hydrogen was pumped off. Then again he added hydrogen and again turned on the pump and watched the return to zero of the incremental resistance. What did he find as a function of temperature? The first slide shows the log of the reaction rate in an Arrehenius plot, versus reciprocal temperature, at around 530°K, which is apparently the Curie point of the nickel film; bulk nickel, of course, has 630°K. But it is well known that nickel oxide films, excited or something like that, have a lower Curie point. So at that temperature he sees a deviation from the straight line. Assuming that a straight line indicates that the activation energy isn't changing appreciably, he then plots the difference of the intercept at these various anomalous points minus the intercept of the straight line divided by the intercept of the line, which gives a measure of the deviation on the prefactor of the Arrehenius formula and that plot is shown on the next slide. You see that there is a 50% dip in that prefactor near the Curie point, of width about 50 degrees on either side of the Curie point. Also he looks for the shift in the Johnson noise but

SUHL (Continued)

had trouble with (1/f) effects characteristic of nickel films. Nevertheless he does seem to see some non-Lorentzian features in the noise at higher frequencies. The time constant is quite long, about 30 seconds. At time less than 3 seconds he finds some non-Lorentzian features and these probably indicate some interesting intermediate stages in the desorption reaction. We hope that we will be able to perform a spectroscopy of catalytic reactions using these noise measurements but that is still some time off. On the theoretical implications, first of all, how is a chemical reaction described? The various reactants are described by the coordinates of the ionic core. You calculate the ground state energy of the outer electrons as a function of the positions of the various cores assuming the cores not to move because they are rather heavy. This is known as the Born-Oppenheimer approximation and it yields the ground state energy as a function of all the core positions. In other words, the ground state energy may be regarded as a hyper-surface in the space of the core coordinates. Different chemical compounds have different minima in the energy surface. A reaction occurs when, because of Brownian motion, the representative point at one minimum describing two compounds penetrates the saddlepoint to the second minimum. For energetic reasons the favored path for the reaction goes over the saddlepoint between two adjacent minima.

So this Brownian motion is very nearly one dimensional going along this favored path. X is the distance along the reaction path. Here is a minimum attributed to chemical A, and another to the other chemical C and between them there is a saddlepoint with height denoted by V. Now we want to know what the formulae are for the reaction rate going from A to B. The Brownian motion is activated and stabilized by interaction with the heat bath. If there were no heat bath to exchange energy, the reaction would not occur. The heat bath in the case of heterogeneous catalysis is presumably the substrate. I define the curvatures of the potential along the reaction path at the lower minima and at maximum as those of two oscillation frequencies ω_A and ω_B. As in all thermally activated processes the reaction rate is given by the usual Arrehenius formula with a barrier factor and with a prefactor, noted in red. As, in many of the experiments, the activation energy did not seem to change, I decided to look at the details of that prefactor using a theory of Kramer's dating back to the 1940's. He computed a series of chemical reaction rates and, although many more detailed calculations have been made since by Karplus and Marcus, there has not been a paper giving a compact overview of the field since then. Kramer's theory treats the chemical reaction as a Brownian motion by means of the so-called Fokker-Planck Equation; he can't solve the Fokker-Planck Equation rigorously under all conditions but he can formulate this prefactor under three different conditions, characterized by a friction constant η, characterizing the friction present in all Brownian motion.

SUHL (Continued)

There is an effective friction constant that is related to the random force correlation function, the random force exerted by the substrate on the chemical. There are three ranges of this friction constant that determine the prefactor in the Arrehenius factor, for the small values, and the intermediate values, and the large values. In the intermediate range, the prefactor is totally independent of the friction constant, in other words totally independent of the dynamics of this interaction, of the chemical, that is of the heat bath. That is the famous Eyring range and in that range the Eyring absolute rate theory applies, and it is somewhat iconoclastic to question it at all. However, I humbly suggest a catalyst may cause the experiment to move out of the Eyring range. ω_B is the curvature at the top of the barrier, ω_A the curvature at the bottom of the minimum, ΔV the height of the barrier. Catalysts cause the barrier between the agent and reaction products to lower so this ΔV gets smaller. Then the curvature at the top of the barrier plausibly also gets much smaller so that ω_B decreases. In the catalytic reaction the range of applicability of the Eyring theory certainly shrinks; it contracts both from below and above. And so it is perhaps not entirely implausible that one is outside the range. Finally, I would like to make one remark that this friction constant plays an important part, if we are right in our conjecture, that maybe the Eyring theory doesn't apply to all stages of the reaction. That friction constant can be calculated by a trick. On the one hand you calculate the response of the reagents to an external disturbance, from the Fokker-Planck Equation, that is from the Brownian motion equation, and on the other hand, you can also calculate it from the so-called Kubo response formulae which are widely used in solid state physics. Newton's third law relates the response of the reactants to the response of the substrate with which they are in interacting, gives the force on the reagents due to the substrate; remember the friction has to do with the force-force correlation function; the force exerted on the reactants is of course related to the force exerted by the reactants on the substrate and that in turn is related to the fluctuations in the substrate. So we have two formulae; one in the case when the coupling has to do with charge fluctuations alone, just a friction coefficient η times the effective mass in this space of the agent. The friction coefficient is related to the charge-charge function of the substrate, the correlation of the charge fluctuations in the substrate which undergo anomalies near ferro-electric transitions for example. On the other hand, in the spin case, the reactants acquire some slight free-radical character; there can be a coupling between the free spins of the reactants and the spins of the substrate so that the friction coefficient is related to the spin-spin correlation function of the substrate, which in turn is related to the paramagnetic susceptibility of the substrate by the fluctuation dissipation theorem so that you might expect some dramatic effects, if all this is true, near phase transitions. The question may be raised now, should this work be funded by government agencies and particularly ARPA. My reply to that is to draw on an analogy to superconductivity. In 1957, the BCS theory has not led to the development of a single high temperature super-conductor, and we do want high temperature super-conductors for super-conducting transmission. The theory has not led to that at all. The reason is simply that the complexities of

SUHL (Continued)

actual high temperature super-conductors are such that these simple, almost microscopic model theories, even though they claim to be microscopic, just didn't have a chance. But nevertheless the theory of super-conductivity has given rise to totally unexpected developments, for example, to the Josephson effect, that had some technical implications and applications; it has led to a much deeper understanding of so-called type 2 superconductivity that may one day help us with the construction of superconducting transmission lines. The same might happen from basic studies of catalysis. Perhaps it will not help us to design more effective catalysts in the foreseeable future but it may have all kinds of surprising spin-offs for surface chemistry and maybe for catalysis. So I do believe it is certainly worthwhile.

Khalafalla: The increased catalytic activity at or near phase transitions has been extensively reported by Professor Irvid Hedvall of Gothenburg University, Sweden, and is commonly referred to as the "Hedvall effect." Lately, we have attributed the synergistic effect of quartz near its (α, β) transition point on the conversion of hematite to magnetite to an increase in the activation entropy. These catalysts may indeed be called catalysts of the second kind, to distinguish them from ordinary catalysts of the first kind which function by lowering the activation energy. Information is sometimes defined as "negentropy." Activation entropy has often been called, "superinformation," hence catalysts of the second kind provide superinformation on the surface by increasing the activation entropy and lowering the "ignorance barrier."

Suhl: The entropy has to do with motion at right angles to the reaction path or to internal motions of the reactants themselves, and of course an anomaly may be related to an extra entropy effect. To convince us of that, however, at the Curie point there should be a substantial change in the whole energy surface, and I just don't see that happen. Paterman tried to interpret his data on that basis, and he found he had to assume some absolutely ridiculous behavior of the entropy as a function of temperature. So, while in some cases, this interpretation may work, my own predilections are for the prefactor.

Huff: I was curious as to how you made your aluminum oxide films. Are they by thermal-oxidation or by vacuum deposition?

Suhl: I believe it was made by deposition.

Huff: Can you give me anymore information on how that was made?

Suhl: No, but if you leave me your address, I will get our experimenter to send it to you.

Huff: Have you tried using field emission electron microscopy to study the changes in the surface of this film as it went through the transition?

Suhl: No. We have only just started this work about two or three months ago. We hope to do all kinds of things, but we haven't got to that yet.

Burwell: How much difference will changing the curvatures make from the Eyring middle value? What kind of effects will be involved?

Suhl: Well, the curve of prefactor versus the friction coefficient goes like this, but some people think it goes like this (indicating). Now, there is an enormous range in which the rate is totally independent of friction coefficient. But, after decreasing curvature of the barrier it begins to look like this (indicating again). Now, if you ask to quantify the statement, "The Catalyst Lowers the Barrier," one can only state qualitatively that there is a reduction in curvature accompanying, similar to that in the famous Constable effect. For a given family of reactions on a given catalyst, the Eyring plot seems to intersect in a related region, and, has to do with accompanying changes in curvature and barrier height. Also, the entropy change is proportional to the lowering of the barrier height. We are studying this in a simple system of three delta functions for barriers and valleys assuming them to be traversed by a single electron. We do indeed get such an effect. Perhaps at some future date, we may be able to say how much the Eyring coefficient changes.

Burwell: But, it might easily be a factor of ten I would guess.

Suhl: Oh yes.

McCormack: I suspect you are being much too humble about the utility of the work you are doing. I have an organic background and am somewhat naive in techniques that you are using. On the other hand, I look at things from analogies and diversities of sources. The literature of polography says solid electrodes accomplish many of the things that catalysts can. Metal reduction processes show somewhat similar behavior. Everything points to the importance of electron transport processes in the surfaces of these operations. We know very little of the band

SUHL (Continued)

structure of catalysts and how electrons move from here to there. Polography actually measures the potentials involved and fixes some aspects of electron tunneling and transport processes, and we need to know a lot more to understand what happens.

Voice: I was just going to ask for the name of your Contract Monitor of NSF.

Suhl: Our theoretical contract is sponsored by the Air Force, although I am trying to change to NSF next year. The experimental work has begun to be sponsored by NSF this year and the monitor is Budnik.

Wise: The literature of catalysis by alloys was old already in the 50's, generating a great deal of excitement about filling of d-bands with s electrons in Group 2 metals. Even in experiments above the Curie temperature, gradually filling d-bands will produce anomalies, so that the theoretical work should take into account, even in the absence of the Curie effect, that such anomalies exist and that some of these anomalies are related to the entropy change itself.

Suhl: I shouldn't have emphasized phase transition as much as I did. Filling the d-band causes various things to change and one very important thing that changes is the paramagnetic susceptibility. Now, these Russian experiments that I referred to have nothing to do with phase transitions, but demonstrate that the change the magnetic susceptibility of the substrate causes enormous changes in reaction rates without causing any change in

SUHL (Continued)

in activation energy. If you have several parameters available, and only one datum, you can always shift the blame to one parameter or another.

Wise: I must tell you the nickel-copper-system is unsuitable for analysis because it does not form homogeneous solutions. The classical work by Eley and Couper on palladium-silver shows that would be a better choice.

Suhl: I am aware of that work. And there again there were strong anomalies observed as a function of filling of the d-band.

Wise: With constant activation energy in the range from 0 to 60 atomic % Ag and therefore variations in activation entropy.

Suhl: Now, you can interpret it as entropy. I prefer to interpret it as defect.

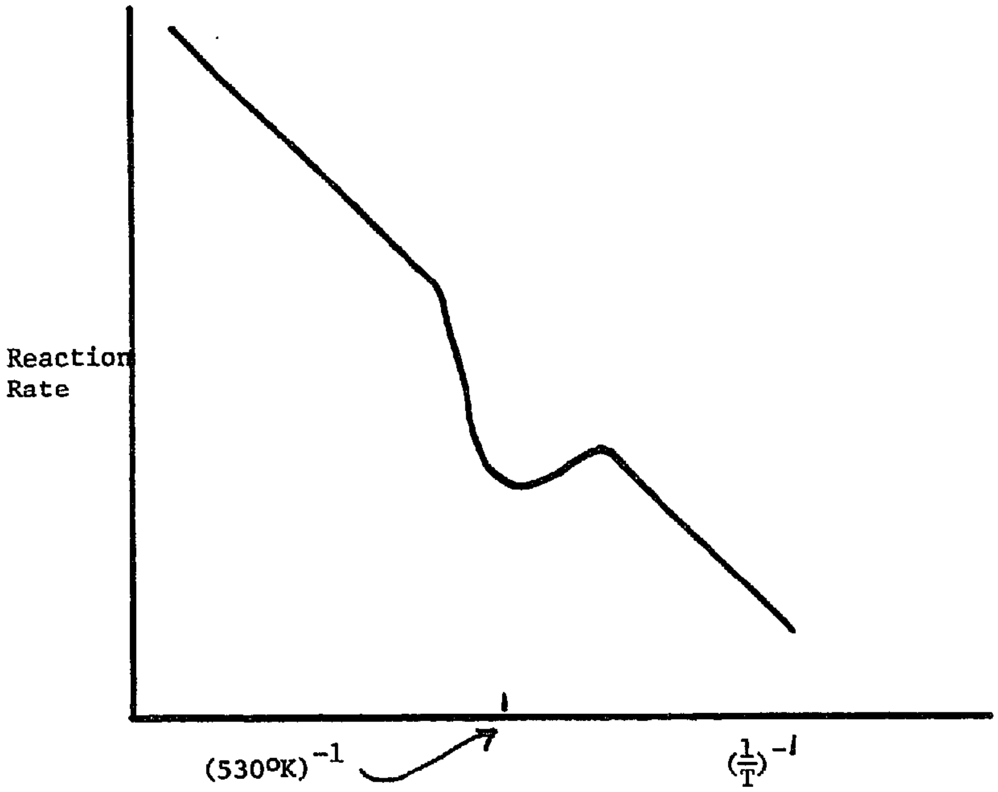
Lauriete: I just want to bring up another entropy phenomenon that has been discovered recently. We are interested in hydrogen storage at Brookhaven in the metallurgical field. We are well acquainted with the stability of titanium hydride. Brookhaven has alloyed titanium with iron, and when this is done, the hydride is a very metastable compound. As a matter of fact, it doesn't take very much heat to disassociate the hydrogen from the compound and when alloyed with iron; it becomes entirely different. This is an example of an alloy changing the characteristics of the compound drastically. The same thing is true for magnesium. We are searching for alloys that will have a low-energy state for absorbing hydrogen.

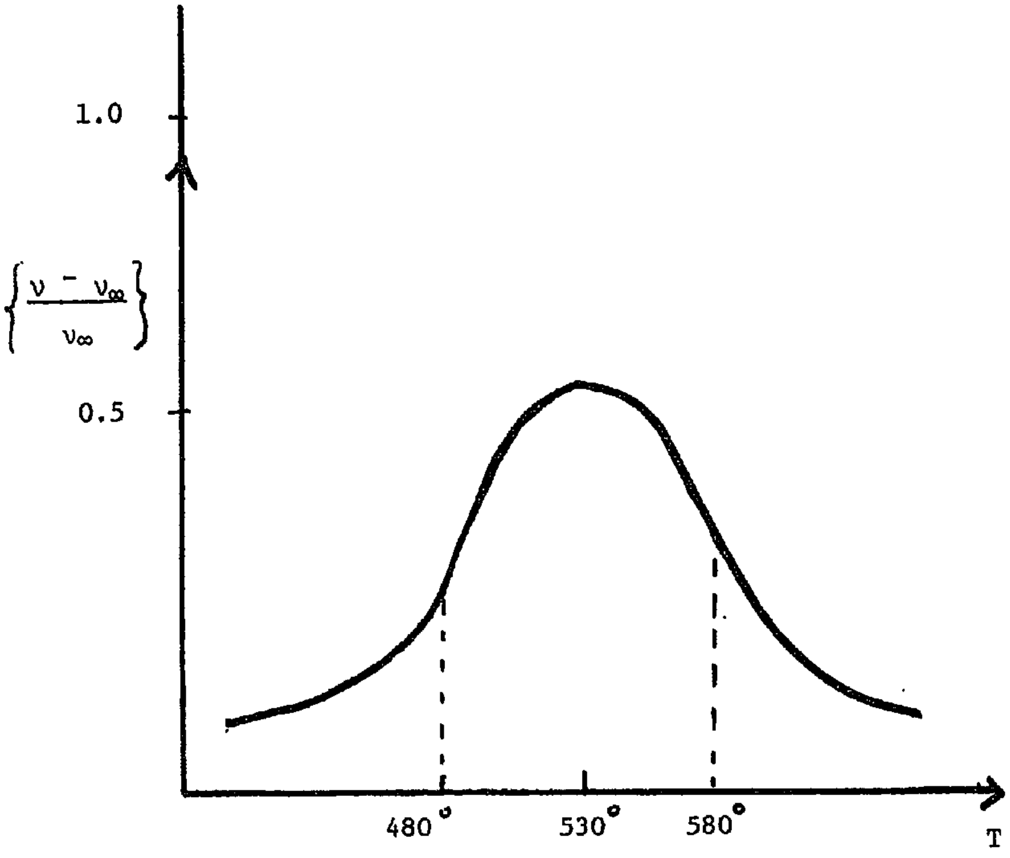
L. Libby: If I understand you, Harry, your theory is very similar in many ways to Gamov-Guerney-Condon tunneling and to the liquid drop fission model.

SUHL (Continued)

These are very powerful precedents. But in order to predict something you must be able to compute those two curvatures at the top and the bottom. Do you know how to do this?

Suhl: Yes, we have formulae which predict the energy surface at these relevant points over the thermal bath degrees of freedom of a certain Boltzman factor. So we have in principle, the formula for computing. In the actual computation, approximations will have to be made and the recent work of Schrieffer and his group promises to give an outline of what has to be done.


Reaction Rate
(530°K)$^{-1}$
$(\frac{1}{T})^{-1}$


1.0
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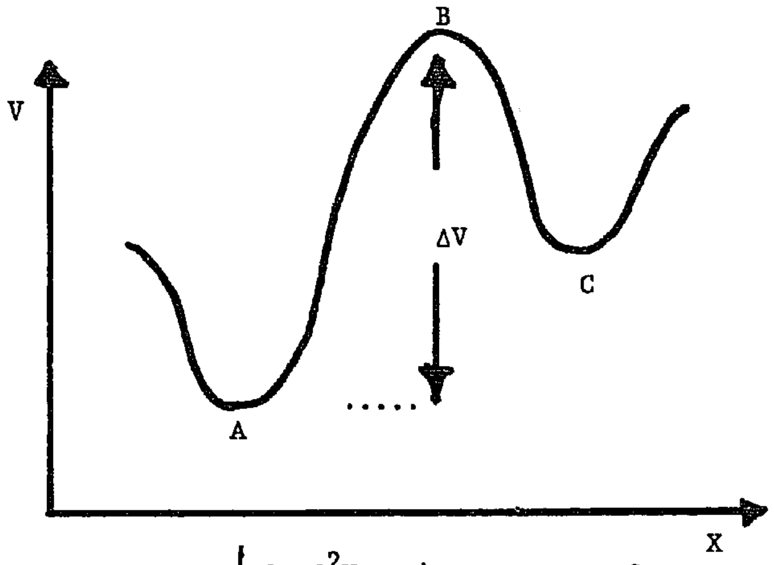

$$\left|\frac{2}{M}\frac{d^2V}{d_x^2}\right|_{X=A} = \omega_A^2$$

$$\left|\frac{2}{M}\frac{d^2V}{d_x^2}\right|_{X=B} = -\omega_B^2$$

Reaction rate:

$$k = \nu e^{-\nabla V/k_B T}$$

1

KRAMER'S THEORY (1940)

$$\nu = \frac{\Delta V}{k_\beta T}\eta \quad \text{for } \nu < \omega_A\ A_B T/\Delta V$$

$$\nu = \omega_A \quad \text{for } \omega_A\ k_\beta\ T/\Delta V < \eta < \omega_B$$

$$\nu = \frac{\omega_A\ \omega_B}{2\pi\eta} \quad \text{for } \eta > \omega_B$$

Eyring absolute rate theory (1932)

Range of applicability of Eyring theory:

$$\omega_A k_\beta T/\Delta V < \eta < \omega_B$$

2

NEW TECHNIQUES NEEDED IN CATALYTIC RESEARCH

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I interpreted my duty as given to me by Joe, not as the duty of inventing new techniques for catalysis like a gamma-ray laser, but rather to tell you how a new technique gets to be used in catalysis. So it's a case study if you wish, and it's a story. It started ten years ago.

I was in Berkeley at the time, and I was driving to the airport with my colleague, Bob Connick, and I told him about the terrible problems we had to study these highly-dispersed, metal supported catalysts. The metal in very small particle size was very elusive, and we didn't know how to tackle that. He said, why don't you go and talk to Dave Shirley who is doing Mössbauer spectroscopy. At that time, Mössbauer spectroscopy was about five years old; I had not heard about it. So I did what Bob Connick recommended, and Dr. Harkins who was working with me at the time started to take some spectra of Mössbauer spectra of platinum. It had not been done before; the result was most disappointing, because we could not really get enough resolution from the various spectra obtained of various platinum salts, and we gave up on platinum.

Professor Parravano was visiting at the time and became interested and started some work with supported gold, with encouraging results.

At that time I moved to Stanford and decided to get equipped to measure Mössbauer spectroscopy of iron.

With DOD money (Army) we built a spectrometer.

From the Mössbauer iron line, we get information on the Debye temperature of the surface, the lattice dynamics. From the position of isomer line or chemical shift of the line, we get information on the various electrons, therefore, also on oxidation states. For instance, we studied $Fe^{2+} \rightleftarrows Fe^{3+}$, reversible oxidation-reduction in zeolites and concluded that these samples should act as very good oxidation catalysts. We decided to oxidize hydrocarbons in the presence of ammonia to avoid cracking on the acidic part of the zeolites. We did anoxidation of propylene and found a very active and selective anoxidation which is not commercial but interesting. The splitting of the line gives us information on the symmetry of the environment and that was quite useful in our work to locate the Fe^{2+} and Fe^{3+} ions in the correct sites in the zeolite.

Thus, we can decide whether iron is at the surface or in subsurface of a very well-dispersed sample, and hence the number of iron atoms in a given sample that are surface atoms, if the dispersion of the iron is sufficiently high.

Finally, from the magnetic hyper-fine splitting, we can study magnetic effects and this we did on an old catalyst that we inherited from Professor Emmett, a singly promoted iron catalyst, to try to find out whether the iron was really iron, and it is, as all people have decided in the past. But, also, we have found information on the location of the alumina promoter which, we think, is largely unreduced in very small x-ray undetectable particles inside the reduced metallic iron crystallites.

Now, finally, following the ferro-magnetic super para-magnetic transition by means of this magnetic hyper-fine splitting, we get information on particle size.

I have listed some of these advantages of Mössbauer spectroscopy on iron. Most important is that we can perform studies under actual conditions of catalytic activity such as high-pressure or in the liquid phase and, such as with working electrodes in an electrolyte, looking at the surface of the electrode.

We have been limited to iron compounds at the moment but we now are tooling up to study gold, the spectra of which require liquid helium temperature, and of course, that's not quite under normal catalytic conditions. There are, of course, challenging possibilities to the techniques of Mössbauer spectra to other isotopes and Leona Libby alluded to this a little earlier this morning. Finally, as an example of our recent studies, we deal with the very small particles - 50% dispersion of metallic particles in alloys of iron and platinum; we think that we can actually use iron as a probe in very small concentration in the small particle of Fe-Pt, so that the iron tells us what's happening around it at the surface. We can count the number of surface iron atoms and determine the surface composition changes under conditions of chemisorption, which we have done, and under conditions of catalysis, which we plan to do. The surface of a catalyst is a steady-state composition of the surface as dictated by the reaction that proceeds on that surface. It is one of the well-known documented dogmas of Carl Wagner, that he has studied over the years with his collaborators at Göttingen.

Very few people are working with Mössbauer spectra but I have very able students who will continue, I hope, to work in this field. There are many problems even with iron. The moral of the story is that it took about fifteen years from inception of the technique by Mössbauer to get where we are at this moment and that's too long. We can be speeded up by better funding I'm sure. The second conclusion is that each new technique is highly specific and can be applied to solve only certain very pin-pointed problems in catalysis. I don't think that any tool can be considered universal.

The third conclusion is that development of methods of surface analysis are very promising for catalysis, and there are many techniques which must be developed. You just can't send your samples to somebody, and hope to get intelligent results, so that actually you can't use commercial surface analytical methods routinely. You must have the machinery in your own laboratory, and you must study the conditions of cleaning of surfaces and the proper conditions of study. For instance, at the moment, we are trying to make measurements of the surface composition of an old Fixed-Nitrogen Laboratory iron-ammonia catalyst by Auger electron spectroscopy, but first we have to learn how to clean an iron surface without using iron bombardment, we don't want to sputter the surface selectively. We have to find the proper chemical means to clean the surface.

Now to do these things successfully, we need continuing funding. And the justification, it seems to me, for the Department of Defense to support an effort like surface analysis as applied to catalysis is that surface chemistry has myriads of applications which are vital to an understanding of catalysis. Also, the application of these techniques is related to material science, and the interest in this aspect of catalysis is best described by considering catalysts as materials. These are most interesting materials, and their study is totally independent of the development of new catalytic processes. Their study should be extremely rewarding.

Thank you.

DISCUSSIONS

S. E. Khalafalla: I'd like to know your findings regarding Emmett's doubly promoted catalysts. How is the potassium oxide incorporated with alumina in the iron matrix? At the Twin Cities' Metallurgy Research Center, we found that most of the promoters of the iron catalyst for ammonia synthesis accelerate iron oxide reduction with carbon monoxide.

M. Boudart: The picture we have is the classical picture as developed by collaborators of Professor Emmett. We have a crystallite of reduced iron, we have a skin with holes in it, with promoters at the surface and as has been reported recently by Solbakken and Emmett, some of the alumina is inside the crystal. It is unreduced, and it must be, according to our Mössbauer spectra, of very small particle size as it is x-ray amorphous with invisible crystallites, perhaps 10 or 15 Å. I don't know anything about the potassium.

S. D. Worley: What was the pressure around the sample in your Mössbauer work?

M. Boudart: We don't need beryllium windows and this is part of a conventional high-vacuum system, and the samples are in the atmosphere that we are interested in, very frequently at atmospheric pressure, for example in hydrogen or oxygen; or we do ammonia synthesis on the samples at atmospheric pressure because it's convenient.

S. D. Worley: I wondered what the background pressure was in the instrument.

M. Boudart: We can evacuate, but the work itself is done in the presence of gases.

S. D. Worley: The gamma-ray goes right through the gas.

M. Boudart: That's the point. We could operate in the liquid phase if we wanted to.

W. K. Hall: I'd like to comment on the effort required to put any new tool into use. The same thing applies to the use of tracers in the study of catalysis and catalysis systems. There are usually not straightforward techniques but you get led from one experiment to another, and finally to the right experiment, which produces meaningful information. The Defense Department will benefit from studies on the surface chemistry of catalysis.

S. D. Worley: Suppose a person was starting up a new laboratory in catalysis. Could you estimate of what it would take to equip that laboratory to do any kind of reasonable work.

M. Boudart: The first prescription would be to build a conventional volumetric adsorption system to measure physical and chemical adsorption. After that, you can add anything.

Hightower: Do you think 100 thousand dollars is a reasonable figure?

M. Boudart: It's not too much.

Professor Suhl: What is a primitive and simple reaction that newcomers in this field could study.

M. Boudart: The reaction, $H_2 + D_2 \rightleftarrows 2$ HD, takes place on several different catalysts at liquid nitrogen temperature, with an activation barrier quite small, otherwise nothing would happen. It takes place on transition metals and chromium oxide, nickel oxide, and magnesium oxide, in the total absence of any substance containing d-electrons.

J. Hightower: Perhaps one should begin with more complex molecules which offer more information. With the simple $H_2 + D_2$ to HD exchange, there may not be enough information available to describe the picture completely. Consider ethanol dehydration for which the only product is ethylene. Both dehydrogenation and dehydration can occur but with dehydration, only ethylene is the product. A more complex alcohol, e.g., secondary butyl alcohol, forms several different products and, perhaps, from the distribution of products one could better determine what happened on the surface. There are these two philosophies and both should be pursued.

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Voice: What other elements are useful in Mössbauer spectral analysis?

M. Boudart: Platinum is not promising at all. Gold, ruthenium, tin and europium are all right. We can use iron as a probe. Perhaps, there are ways to excite the nuclear levels in the future, and then there would be many more isotopes that could be investigated.

L. M. Libby: Maybe it would be useful to provide an information service about particle physics methods at all energies to catalyst scientists, for studies of surfaces by methods that are not being used today. The particle physics methods include, for example, radiation physics, particles from Van-der-Graafs, cyclotron beams, elementary particle scattering at all energies and heavy ion implanation on surfaces. Information on these methods, the corresponding accuracies, the milligrams or the micrograms per square centimeter amenable to analysis in surfaces, may be useful to know, and especially to tell who are the people who practice these technologies and who will want to make measurements useful to the real world. Particle physics has long been aloof, but should be solving these important problems.

Haensel: Leona, everybody wants the real problems, because that's the way they get money. There's nothing wrong with it, but some of the basic work may have to go by the side in order to do this.

Dr. Libby: Well, for example, we asked people at Brookhaven to measure the oxygen - 18 to 16 ratio on a very thin film of less than a milligram per square centimeter, and they did it. We worked very closely, and they were delighted. But there are many, many more examples, which I won't take time for. I'm asking you if such a service would be valuable to catalyst scientists. You can begin to talk to such specialists.

Dr. McCormack: Can particle methods be used also to measure bulk properties, or are they restricted to surfaces?

Dr. Libby: Yes, particle beams can probe bulk material to any desired depth, but since we've been mainly discussing the properties of surfaces, and thin layers on those surfaces, that's why I spoke that way.

Dr. McCormack: You say we can restrict those techniques to the surface layers?

Dr. Libby: Yes, by restricting the energy of the radiation of the particle beam. There is a finite range to any monochromatic particle beam.

Dr. Hall: I'd just like to say that such a service can't hurt anything, but I'd like to recommend something that I consider a much more important matter, namely, the catalyst bank, which was mentioned by Dr. Heinemann earlier.

Dr. Burwell: The Commission on Colloid and Surface Chemistry of the International Union of Pure and Applied Chemistry Commission in collaboration with the National Physical Laboratory and the Society of Chemical Industry undertook an examination of standards for surface area, four of which are available from the National Physical Laboratory (Teddington). Consideration is being given to extend this service to catalysts.

J. Hightower: All of these topics will be discussed in more detail, when we talk about the Catalyst Institute this afternoon.

Dr. Burwell: The US-USSR International Cooperation in catalysis sponsors a storage of catalyst samples and testing by both sides.

<u>Professor Suhl</u>: Could not such a laboratory be established at Brookhaven?

<u>Dr. Libby</u>: Yes, but other laboratories also have specialities. Goulding at Lawrence Berkeley has a technology developed for looking at nuclear radiations and it's a very shallow technology, namely, it measures only surfaces, and the depth of the surface to be examined can be controlled.

<u>Boudart</u>: Exchange of information over the past year, shows that a number of physicists and material scientists are getting interested in catalysis. Catalyst scientists are aware of what goes on. We are desperate, and any new technique that appears on the horizon, we know about; but there is a good deal of education to do in the materials community. We tried to do this at Stanford last Spring in a workshop, and it should be followed-up.

INFORMATION OBTAINED FROM MÖSSBAUER SPECTROSCOPY

LINES	PARAMETER STUDIED	INFORMATION OBTAINED
1	Intensity	Strength of bonding
	Position	Electronic environment (oxidation state, covalency)
2	Separation	Symmetry of environment
6	Separation	Magnetic fields at nucleus
	Shape vs T	Particle size

MÖSSBAUER SPECTROSCOPY APPLIED TO CATALYSIS

ADVANTAGES

All atoms in absorber contribute to spectrum
X-ray amorphous samples can be studied
Small particles pose no limitations
Particle size information
Becomes a surface technique for small particles
Liquid phase
Relatively cheap and rapid
Non-destructive
In-situ studies under normal conditions of catalysis

LIMITATIONS

Limited number of Mössbauer active nuclei

APPLICATION OF MÖSSBAUER TO FePt/C CATALYSTS

The 10-20Å particles are alloys

Surface atoms can be observed

Changes due to chemisorption occur

Surface composition could be determined

Enrichment in fraction of iron at surface after 300°C oxygen treatment

CATALYSIS IN SYNTHETIC RUBBER PRODUCTION

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After World War II, the U.S. Government sold to private industry the country's facilities for rubber production. One of the largest of these is the Port Neches complex, where a large butadiene plant jointly owned by B.F. Goodrich and Texas-U.S. Rubber supplies two adjacent SBR plants each owned separately by Goodrich and Texas-U.S. The combined production of the two rubber plants is 400,000 tons of SBR based chiefly on emulsion polymerization.

Subsequently, through the utilization of metal alkyl catalysis, a whole new array of monomer combinations became possible with the formation of stereoregular polymers. These catalysts, in the case of isoprene, led to the duplication of natural rubber itself. In other cases, elastomeric and thermoplastic products are now produced to an extent never before thought possible due to these advances in catalytic polymerization initiators.

The dynamic growth of synthetic polymers into one of the major segments of the U.S. economy[1] is intimately related to the science of catalysis, not only in the catalytic initiation of the polymerization process itself, but in the synthesis of its monomeric building blocks from basic hydrocarbons.

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[1] Slide #1

The use of catalysis in the polymerization process is a vast area of technical investigation continuously being pursued as new catalysts are synthesized and their effectiveness increased through a variety of techniques. The polymeric product, the polymerization process, and the type of polymerization mechanism employed, all dictate the kind of applied research utilized in the evolution of these catalysts. Since much of this involves solution or aqueous polymerization practice, the enhancement of catalytic effectiveness generally involves the incorporation of functional groups to alter catalyst compatibility between monomer, polymer and solvent, non-solvent combinations. This area of catalysis is aimed at increasing, for example, the effectiveness of the catalyst per pound of polymer produced. This is an area of investigation critical to the economic viability of these products.

The rapid growth of polymer applications and the associated applied research aimed at the commercialization of a particular proprietary process or product has led to a serious disparity between the theoretical elucidation of both polymers and catalysis. This is usually the expected situation. The continuing growth of synthetic polymers and their versatility and applicability to so much of our social and economic welfare, dictates that steps should be taken to provide for a better utilization of our academic research facilities toward the practical solution of some of our most urgent national problems. Among these national problems, our current energy crisis and its impact and implications on the entire polymer industry and the national economy is critical. Studies in catalysis can contribute to the optimum usage of our valuable raw materials, environmental pollution problems, and the growing contribution of polymers to our standard of living.

In most of our universities, both the area of polymer science and catalysis are neglected fields of instruction and research. This is undoubtedly due to the common need in both areas for significant interdisciplinary interaction. If meaningful steps could be taken toward a fruitful combination of these disciplines, a more effective utilization of our combined talents could be realized and much wasted repetitive effort eliminated for the common good. This could be accomplished through appropriate national direction toward the effective cooperation between the science, engineering and manufacturing elements of the community.

Today, almost all polymeric products are based on a few petrochemically derived hydrocarbon monomers from C_2 to C_5 which are transformed into the monomeric building blocks via a variety of catalytic processes. The relevance of these petrochemical feed stocks to synthetic rubber can be seen when one realizes that approximately 5 gallons of crude oil are required per single passenger tire.[2] This would constitute an estimated 2% of the total U.S. crude oil production for 1973.

Conjugated dienes such as butadiene, the major component of Styrene Butadiene Rubber, [3,4] are the key components of elastomeric polymers. Both butadiene and isoprene are obtained by the catalytic dehydrogenation of butylenes and t-amylenes respectively. The process is endothermic and is a high fuel and energy consuming operation requiring large volumes of steam as a diluent. The unsaturated feeds are obtained by distillation and extraction from refinery feed stocks. Thus the tire industry must compete with the energy market and in many cases, it is dependent for its raw materials on the by-products of the petroleum or petrochemical industries.

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[2] Slide #2
[3] Slide #3
[4] Slide #4

The classification of catalysts according to their use in various processes readily illustrates the key role these play in monomer sythesis.[5] While dehydrogenation shows this relative to the current production of butadiene and isoprene, other synthetic routes are available. National direction and guidance of catalytic research toward the elucidation of fundamental theories of catalysis in these processes could contribute significantly toward our national welfare.

The need for meaningful contributions in the area of catalysis which could significantly influence the efficient utilization of our raw materials is obvious. An area where the need for catalytic research could be most helpful is in challenging the theoretical inorganic disciplines to consider the role of these surface activated catalytic sites under actual reaction conditions, not relative to the organic chemistry but rather to the complex nature of the inorganic species. A better understanding of just how these activated inorganic complexes interact with each other to promote these transformations are basic to the understanding of the catalytic theory of a particular reaction. The combination of conducting these reactions with or without tagged reactants, at the desired reaction conditions in appropriately modified apparatus to measure these surface effects with sophisticated instrumentation is a real test of ingenuity. It requires the expertise of a particular process being studied and the theoretical contribution of the complex chemistry involved -- a rare combination of disciplines.

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[5] Slide #5

What has just been discussed relative to the synthesis of a few individual monomers and their elastomeric products is typical of the majority of the synthetic polymer industry. Its dependence on the availability of petrochemical feed stocks for its monomers relative to our current energy demand requires a concerted effort in catalytic research to improve our existing processes or provide practical alternates. This can be accomplished by the combined interaction of a willing and cooperative scientific community interacting for our mutual benefit. We have the capability to accomplish this but need national direction to do this as rapidly and efficiently as possible.

L.M. Libby: Do you recommend study of activated organic complexes of rubber production, as well as inorganic complexes, to be supported for intensive research?

H.J. Essig: I'd like not to limit it to rubber production. There are a number of areas, for example, propylene oxidation to make acrylic acid, for which the catalysts that are being used have been developed and immediately put into commercial production of the product, but the basic understanding of what other inorganic combinations can be put together for better catalysts, and how these function, is lacking. The inorganic backgrounds are left behind not understood because we are in such a hurry to commercialize these processes, and this is true time and time again.

PRODUCTION OF PRINCIPAL POLYMERS AND METALS IN THE USA*

	1968 (cu ft 10^7)	1973 (cu ft 10^7, est)
Synthetic polymers	400	710
Plastics	260	500
Elastomers	80	110
Fibers	60	100
Steel and Non-Ferrous metals	424	566
Steel	370	500
Aluminum	40	50
Zinc	6	7
Copper	4.5	4.7
Magnesium	2	3
Lead	1.5	1.6

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*Ind. Eng. Chem., 61, (1969)

Slide #1

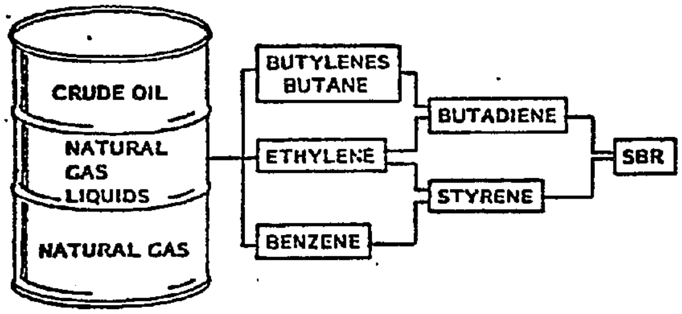
CRUDE OIL CONSUMED PER TIRE

	Crude Oil Gallons
Raw Materials including processing energy	5
Energy consumed in manufacture of tire	2
TOTAL	7

Source: "The Energy Crisis and the Tire Industry", J.R. Hall, President, Ashland Chemical keynote address Akron Rubber Group - Oct. 5, 1973.

Slide #2

SBR RAW MATERIALS



Source: "The Energy Crisis and the Tire Industry", J.R. Hall, President, Ashland Chemical keynote address Akron Rubber Group - Oct. 5, 1973.

Slide #3

"TYPICAL" TIRE COMPONENTS

	POUNDS	PERCENT
SBR	7.8	26.0
Polybutadiene	2.6	8.7
Isoprenic Rubber	1.9	6.3
Butyl or Chlorobutyl	1.0	3.3
Carbon Black	7.4	24.7
Extender Oil	3.9	13.0
Fibers (Including Bead)	4.0	13.3
Chemicals	1.4	4.7
TOTAL	30.0	100.0

Source: "The Energy Crisis and the Tire Industry", J.R. Hall, President, Ashland Chemical keynote address Akron Rubber Group - Oct. 5, 1973.

Slide #4

CATALYTIC PROCESSES IN MONOMER SYNTHESIS

ALKYLATION
AMMOXIDATION
CYCLIZATION
DEHYDRATION & HYDRATION
DEHYDROGENATION
ESTERIFICATION
HALOGENATION & DEHALOGENATION
HYDRODEALKYLATION
HYDROCRACKING
HYDROGENATION & HYDROGENOLYSIS
INTERESTERIFICATION
ISOMERIZATION
OXIDATION
OXYCHLORINATION
OXYDEHYDROGENATION
OXO-PROCESS

Slide #5

CATALYSIS IN POLYMERIZATION

FREE RADICAL TYPES (peroxides, hydroperoxides, redox systems, etc.)

ANIONIC TYPES - organometallics

CATIONIC TYPES - boron-trifluoride-ethers, etc.

METAL ALKYLS - transition metals and oxides, aluminum or titanium alkyls, etc.

Slide #5a

ELECTRODE CATALYSIS IN FUEL CELLS

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The characteristics which led to the selection of the fuel cell as a power source for extended space missions, namely its high energy density and its ability to generate potable water, continue to make the fuel cell concept attractive for many space and specialized military applications. Because it is a clean, quiet electric generator which operates with superior efficiency in both small and large sizes the fuel cell could also contribute significantly in many problem areas associated with the national concern for conservation both of energy and the quality of the environment. With these goals in mind, modular fuel cell installations of a few kilo watts to many mega watts have been proposed and are being developed as a flexible source of power complementary to the overall supply.

A wide range of fuel cell configurations which have been experimentally demonstrated could be further developed. These are best classified according to the temperature range in which they operate since this defines the type of electrolyte and to some extent the fuel which can be used. At high temperature,fuel cells with solid oxide and molten salt electrolytes are potentially attractive because the electrode reactions are so rapid that specially catalytic surfaces may not be necessary, and hydrocarbon fuels may be reacted at the anode directly. But to overcome the problems of long term operation in a corrosive environment the development of new structural materials, would be required. At low temperature, i.e. below 200°C, concentrated acids and bases are used as electrolyte and the requirement for corrosion resistant materials becomes less severe though not negligible. However, the ability of the catalyst to facilitate the electrode reaction becomes a major limitation in the performance of the cell. At the present time most fuel cell systems available for either military or commercial use operate in the low temperature range therefore the study of catalytic processes at the electrode interface is a critical step in the continued development of fuel cells.

In fuel cells containing low temperature base electrolyte direct oxidation of hydrocarbons is impractical for the long term because of the concomitant reaction of the product carbon dioxide with the electrolyte, while in acid electrolyte overvoltages associated with hydrocarbon oxidation have proved to be prohibitively high. Therefore, the electrode reactions of interest have primarily been the oxidation of hydrogen and the reduction of oxygen. Both these reactions though extensively studied, are still the subject of debate consequently increased fundamental understanding of their mechanisms can contribute both in the optimization of established catalysts and in the development of new ones. Since electro-catalysts must operate in hostile environments at high temperature it is of equal importance to understand those processes, such as oxidation, electrochemical corrosion and sintering which limit the materials considered as potential catalytic surfaces.

Many of the phenomena which are of concern in the study of reactions at the gas-solid interphase are also important in understanding electro-catalytic processes. Thus the relationship between crystallite size and catalytic behavior which has been extensively investigated for gas-solid interactions, has also been studied for several electrochemical reactions(1-3). For example an examination of the activity contributions of atoms at corners, edges and planes of platinum electrocatalyst crystallites has been carried out for the reduction of molecular oxygen in 1M H_2SO_4. Varying the mean crystallite diameters between 30 and 400 Å caused at least a 200 fold and 30 fold change in the surface densities of corner and edge sites respectively. Deliberate sintering of the platinum crystallites caused growth with a reduction of surface and lattice defects. These catalysts showed uniform activity for oxygen reduction of 0.018 ± .003 mA/real cm^2 Pt at 900 mV (nhe). Moreover, the Tafel slope of the polarization curves had a constant value of 65 ± 5 mV indicating that the mechanism of the reaction did not vary. Platinum atoms at corners, edges, kinks and dislocations therefore are not more active than atoms on the crystallite faces for this reaction. In contrast a similar study of the reduction of platinum surface oxide showed a functional relationship between Tafel slope and oxide coverage which changed with changing crystallite size(2). For hydrogen chemisorption also,significant changes in the relative concentration of the three surface species were observed in potentiodynamic sweep measurements on platinum crystallites of varying diameter (3). Thus only those processes in which a strongly chemisorbed species was formed were sensitive to changes in the morphology of the crystallite surface.

Since practical fuel cell configurations are designed with maximum gas-liquid-solid inter-phase area catalysts of necessity are high specific surface area materials, consequently research on electrode catalysis must focus on processes occurring on microcrystallites. Methods of characterization which have been so extensively developed for the high surface area materials commonly used in gas-solid catalysis must also be developed for catalysts peculiar to electrochemistry. Selective chemisorption and transmission electron microscopy are of limited use in determining the surface area of platinum dispersed on carbon. The former technique presents difficult problems in the pretreatment of the catalyst prior to measurement of any but the cleanest of carbon blacks. The electrochemical potentiodynamic scanning techniques for measuring chemisorption prove to be more effective in this case because surface pretreatment can be successfully accomplished by rapid potential variation (4). In the direct transmission mode of the electron microscope, contrast between catalyst and support is poor. However, using the dark field mode particle sizes determined by the electron microscope correlate closely with electrochemically determined surface areas(5).

The work described here directs attention to some areas of concern for research in electro-catalysis and emphasises that advances in catalyst technology for fuel cells requires increased understanding of the behavior of high surface area materials. Problems exist in the stability of materials, particularly conductive oxides, whose solution would significantly extend the range of surface which could be considered as catalysts. No detailed accounting of specific goals in catalyst development can be made because these will depend on a complex optimization of all operating conditions of the fuel cell and its particular application. Selection might be made from several of the configurations mentioned in the opening paragraphs. The direction of research effort to those areas which bear the greatest promise of practical as well as scientific success will require the closest interaction between engineering development programs and the research laboratory.

(1) J. Bett, J. Lundquist, E. Washington, P. Stonehart, Electrochim. Acta, 18, 343, (1973.)

(2) J. T. Lundquist, P. Stonehart, Electrochim. Acta, 18, 349 (1973).

(3) K. Kinoshita, J. T. Lundquist, P. Stonehart, J. Cat (1973).

(4) J. Bett, K. Kinoshita, K. Routsis, P. Stonehart, J. Cat. 29, 160 (1973).

(5) J. Bett, K. Kinoshita, Electrochim. Acta, 18 (1973).

(6) K. Kinoshita, D. Fornwalt, Micron 4, 99, (1973)

FUELS AND OTHER CORRESPONDING POWERPLANTS

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(Introduction by Dr. Hightower: Dr. Quillian is the Director of the U.S. Army Fuel and Lubricants Laboratory in San Antonio, Texas, but his controbution to this Workshop does not represent official Army nor DOD opinions.)

Joe, thank you for disqualifying my opinions. The wide variation in fuel possibilities and the numerous possible energy transformation systems precludes an in depth discussion of this subject. The subject is important, however, and should be considered by DOD as prerequisite information to any kind of applied catalytic research. This statement does not apply to fundamental and exploratory catalytic research. So, in support of this belief, I shall initially recommend that DOD sponsor still another workshop for the purpose of correlating fossil fuel possibilities with future powerplant possibilities. Such a workshop would be very useful and timely.

In reporting to you on future fuels and their corresponding powerplants, the opportunity is offered to define an additional application of catalysis to DOD interests. The application is to improve the availability of fuels during combat conditions rather than during the peacetime conditions as discussed during most of this workshop. This application of catalysts differs considerably from those to improve the availability of peacetime, commercially available, fuels. For example, catalyst life for combat applications need not be any longer than the duration of the defense conflict. Catalysts need not be economically competitive with commercial systems. Preferably, they should be portable. So this opens up a new avenue of thinking about catalysis processes. Therefore, I plan to limit the scope of my brief discussion to future defense (or combat) fuels and their corresponding powerplants.

This first slide lists the format for my subject --- the fuels preferred, fuels available, and the compatibility of the fuels that are available for use with powerplants.

The second slide lists the fuels preferred according to the fraction output from the refinery. Arbitrary judgement values are shown as poor, fair, and good. LPG fuels have poor climate tolerance since they must be containe in pressurized fuel tanks. Keep in mind that I am referring primarily to fuels for vehicles used within DOD for their mobility requirements, since this is the largest requirement for defense fuels. BTU's per gallon of LPG are poor, around 85 to 95 thousand BTU's per gallon, even though they do have high BTU's per pound --- something like 19.5 thousand BTU's per pound. LPG fuels also have relatively severe safety hazards, but their engine applications are good and they run quite well in turbine and spark ignition engines. The light distillate fraction is the approximate equivalent of gasoline. The climate tolerance of gasolines is fair, but not good to the extent that one must have winter grade gasolines and summer grade gasolines.

BTU's per gallon are improved over LPG, but the fire safety is still poor while engine applications are quite good. The fuels most preferred are the middle distillates; they pour well at low temperatures; they work well at high temperatures; they have relatively good energy density. They also have very good fire safety properties except for their misting tendencies under impact conditions. They have very good engine applications, except for spark-ignition engines. With the heavier distillate fuels there are climate problems; some of these fuels do not have good pumpability properties at low temperatures. Heavy distillates can also cause deposition problems because of the inefficient burning of some of the more carbonaceous hydrocarbon components. Residuals simply accentuate the problems that you will find with the heavier distillates.

Slide 3 categorizes all the fuels that may be made available for vehicle mobility. This slide is not a plot of data. If it were, it would probably be classified information. The curves give hypothetical supply and demand information on fuels required for a maximum, general, non-nuclear war at any point on the earth. The dashed curve indicates the assured supply of petroleum products; and the solid part of the demand curve is partially valid because point A is the true peak value of defense requirements during World War II. Point B is the average requirement during the height of the Southeast Asian conflict, a limited war, and it is appropriate to comment that if it was a limited war, then it represented about 60% of the maximum war indicated by the hypothetical demand curve. The Office of the Secretary of Defense has made some unclassified projections that we will probably not need more than 10 to 12 per cent of the maximum U. S. refinery output for a maximum war, and I have taken liberties with their estimates in order to locate Points C, D and E. Some of the liberties were to assume that OSD meant defense demands from any place on the earth, that they meant finished fuel outputs from refineries in the contiguous United States and that the fuels would have an average heating value of 5.8×10^6 BTU per barrel. Points C, D and E are, therefore, not very reliable. The supplies curve is completely arbitrary. It is defensible only to the extent that it has a configuration similar to estimates of the world petroleum supply capability. Additionally, the year 1971 was chosen for the intersection point of the supply and demand curves. The basis for selecting 1971 was the occurrence of minor difficulties in some fuel procurements for the SEA conflict, plus growing problems in the supply of fuels for peacetime purposes. Surplus supply capability is thus indicated for the years prior to 1971 and deficit supply capability for the years after 1971.

There are three different categories of fuels of interest to DOD - conventional, emergency and long-range. Now and in the years to come, DOD will always go to the refiners and procure commercially available fuels in a conventional manner. These commercially available fuels can come from crudes, coals, shale oils, tar sands, and other fossil sources, even though we are getting only petroleum fuels now. You can appreciate that beyond 1980 and '85 these alternate energy sources will be in the picture. But, as of today, catalysis has not progressed sufficiently to permit the development of finished alternate fuels to supplement those that are commercially available, so DOD must determine what can be used in an emergency if there are not adequate finished fuel supplies of the conventional type. We can use crudes, naphthas, burner oils and possibly a few alcohols from ocean going tankers, and these seem to be about the only emergency fuels that are immediately available to us. Now, these emergency fuels are not desirable as they do not burn well in most internal combustion engines, although some heating oils work quite well in some diesel engines. So we must take measures to eliminate the need for emergency fuels and lead time into the 1980's will be required before we can begin initial use of the long-range fuels indicated on Slide 3. The feasibility of using hydrogen and the possibility of synthesizing hydrocarbons from hydrogen and a carbon source has been discussed by many investigators. Petroleum and coal are included as candidates for long-range fuels by assuming that commercial fuels from these sources will be inadequate and that some kind of mobile petroleum or coal processing equipment can be developed for use at the scene of the conflict to make the supplemental fuels required.

Next, I shall correlate the compatibility of powerplants with conventional, emergency, and long-range fuels.

Slide 4 summarizes the performance of conventional fuels in current and future powerplants. The slide identifies five different engine types that are intended to encompass most of the candidate engine systems. The classic engines, spark, turbine, and the diesel need no explanation. "Stratified" engines, however, should be considered to include such concepts as the Texaco combustion system, the Honda stratified charge method, the Ford PROCO, the Hesselman process, the Witsky stratified charge engine and even the General Motors rotary engine, if rumor holds up that it may indeed have some stratifying capability.

Quillian (Continued)

"External" refers to such cycles as the Stirling, Rankine, closed Brayton, and other heat engine cycles. These powerplant types, therefore, cover most of the candidate prime movers with the exception of fuel cells. Diesels, turbines, stratified, and external combustion engines all run well on middle distillate fractions. Jet fuels are mostly middle distillate too. Spark ignition engines fail on these kinds of fuels, but the classic spark engines are no longer preferred by DOD because they do not have the inherent economy and the reliability that the diesel engines do.

Slide 5 lists the emergency fuels in their probable order of availability, putting residuals first because you will find heating oils not only in tankers traveling the oceans, but also you will find them very frequently in municipalities around the world to power the generator sets or to heat homes. Residual fuels are everywhere, and thus available for use as emergency fuels either by normal procurement, by commandeering, or by whatever means. They should work well in external combustion engines, but suitable external combustion engines have not yet been developed, so the advantage in this engine is immaterial for the present time. Residuals with good fluidity and pumpability at low temperatures will work well right now in a number of diesel engines. Stratified charge engines which may soon come into usage use a direct fuel injection system and should give fair performance on most pumpable residuals. Spark engines and vehicular turbine engines do not work very well on residuals, although most stationary industrial turbines do. Additionally, a few ground turbine engines will give acceptable emergency performance on residuals, but such fuels would not be suitable for aircraft turbines. With regard to crudes, that is the best 40%, I am referring to fuels with 2½% sulfur or less, which exceeds acceptable standards today, but which will run adequately in an engine under an emergency situation. Residium at less than 15% and a pour point at 32°F or lower describes the crudes that show promise for use in diesel and stratified charge engines. Distillates, like jet naphthas and jet kerosines which comprise a fraction of the tanker shipments, are the choice and the least available of the emergency fuels. They work quite well in stratified charge, diesel and turbine engines, but again, not in spark ignition engines. Alcohols are included as emergency fuel candidates because of the possibility that ethyl alcohol may sometime in the next 5 or 10 years become an intermediate between a natural gas source in the Mideast and an alcohol-to-gas reprocessing plant here in the United States. If so, alcohols would be shipped by tankers to the United States, and it is noteworthy to mention that they are about the only emergency fuel that can be used in spark ignition with any degree of success.

Slide 6 describes the compatibility of long-range fuels with powerplants. Synthetic hydrocarbons are shown at the top of the list because it is not likely within the next two or three decades that we will switch to hydrogen as a vehicular fuel. Hydrogen may very well have a key role in the production of synthetic hydrocarbons. With an adequate supply of hydrogen and a carbon source catalysis methods can be used to synthesize hydrocarbon fuels, and that is perhaps the more appropriate way to assure the availability of the most desirable combat fuels as all the engines should work well on synthesized hydrocarbons. Hydrogen and hydrides work well in most of these engines too. People continue to discover that hydrogen works in an internal combustion engine and I don't know why they persist in doing this. The problem is not the challenge of getting it to burn, it is simply that there is a logistics difficulty in transporting hydrogen from Point A to Point B, and especially, that a heavy and massive fuel tank, some two or three times larger than for liquid hydrocarbons, is required. With regard to hydrides, I understand that hydrogen can be stored more densely than in a liquid state, but that it is nonetheless too low in BTU density per unit volume. Hydrazine and UDMH have long been explored and sometimes used for rocket propulsion. These fuels have also been investigated from time-to-time for use in piston engines and they do not do well at all. Ammonia was proposed as a fuel for the mobile energy depot concept of the early 1960's, and our laboratory in San Antonio explored its application as a fuel for spark and diesel engines. It will work in spark ignition engines and turbine engines, but it is terrible in diesel engines and probably will not work well in a stratified charge engine. Alcohols merit the same comments I gave you before for emergency fuel use. Out of respect for Dr. Huff and Mr. Bett, I say these long-range fuels are good candidates for fuel cells and so if you fuel-cell-experts come into your own and produce the horsepower-to-weight-and-volume ratios we need for vehicles, then we have a winner with almost any of these fuels. Well, that's the best I can do in the time allowed, Joe, and, in summary, I want to say that, based on what I've seen thus far, catalysts do appear to have applications to DOD interests. This statement applies to all of the fuel types I've discussed - conventional fuels, emergency fuels, and long-range fuels. For conventional fuels, catalysts can increase the middle distillate fractions. For emergency fuels, catalysts can be used in the

Quillian (Continued)

development of mobile facilities that can be taken to the site of combat. There should be immediate use for a catalytic black box that could be hooked in with the fuel dispensing equipment now used in the field. This equipment consists, of course, of filter separater units that remove the water and filter the dirt out. An additional catalyst system that would accommodate crudes and give them a partial fractionation before use would greatly improve the quality of the emergency fuels. Catalyst applications, therefore, exist for the production of combat fuels as well as for making the future commercial fuels you've been talking about during the course of this meeting. Thank you.

Discussion:

Haensel: About ammonia, this is with non decomposition, or with a decomposition first?

Quillian: This is with the engine doing the decomposition itself.

Quillian: The diesel engine is really handicapped because it takes time to release hydrogen.

Haensel: In other words, you do not have a decomposer first. Instead, ammonia is decomposed to hydrogen and nitrogen, and fed directly into the engine with the ammonia.

Quillian: Yes, but hydrogen is not a good fuel for a diesel engine, the reason being that it has a high auto ignition temperature, and you need a big spark to get the ignition started.

Dr. Hall: Supposing methanol would work in fuel cells, could you build a truck which would run on the fuel cells or would it take a truck to carry the equipment?

Quillian: You want to volunteer the answer to that, John?

Bett: You could build one to run on it. We're not concerned with on-the-road vehicles, but we are concerned with materials handling equipment, and these fuel cells are prime candidates for hydrogen burning with an average power output of between 12 to 15 kilowatts, ideal for a fuel cell for steady power, plus batteries for peaking, even using lead acids as a battery on a conventional truck.

L. Libby: What does it weigh?

Dr. Huff: You might even have to weight it down with lead, because it'll be light.

L. Libby: What do commercial cells weigh per kilowatt.

Quillian: For the Apollo cell, 750 pounds. The PC-3, which is a one and one-half kilowatt cell, thirty volts, is 225 pounds.

Dr. Cohn: How much platinum is required?

Quillian: I'm sorry, I can't comment.

Cohn: Regarding emergency fuels, I lived in the beginning of World War II in Sweden, with very severe problems. A good many cars ran on calcium carbide and ran quite well.

Quillian: We considered that; we also considered the German system of destructive distillation. The mobility is so impared, that we felt that this would be used as it was in Germany, for civilian use and not for combat, so we've rejected this as an emergency possibility.

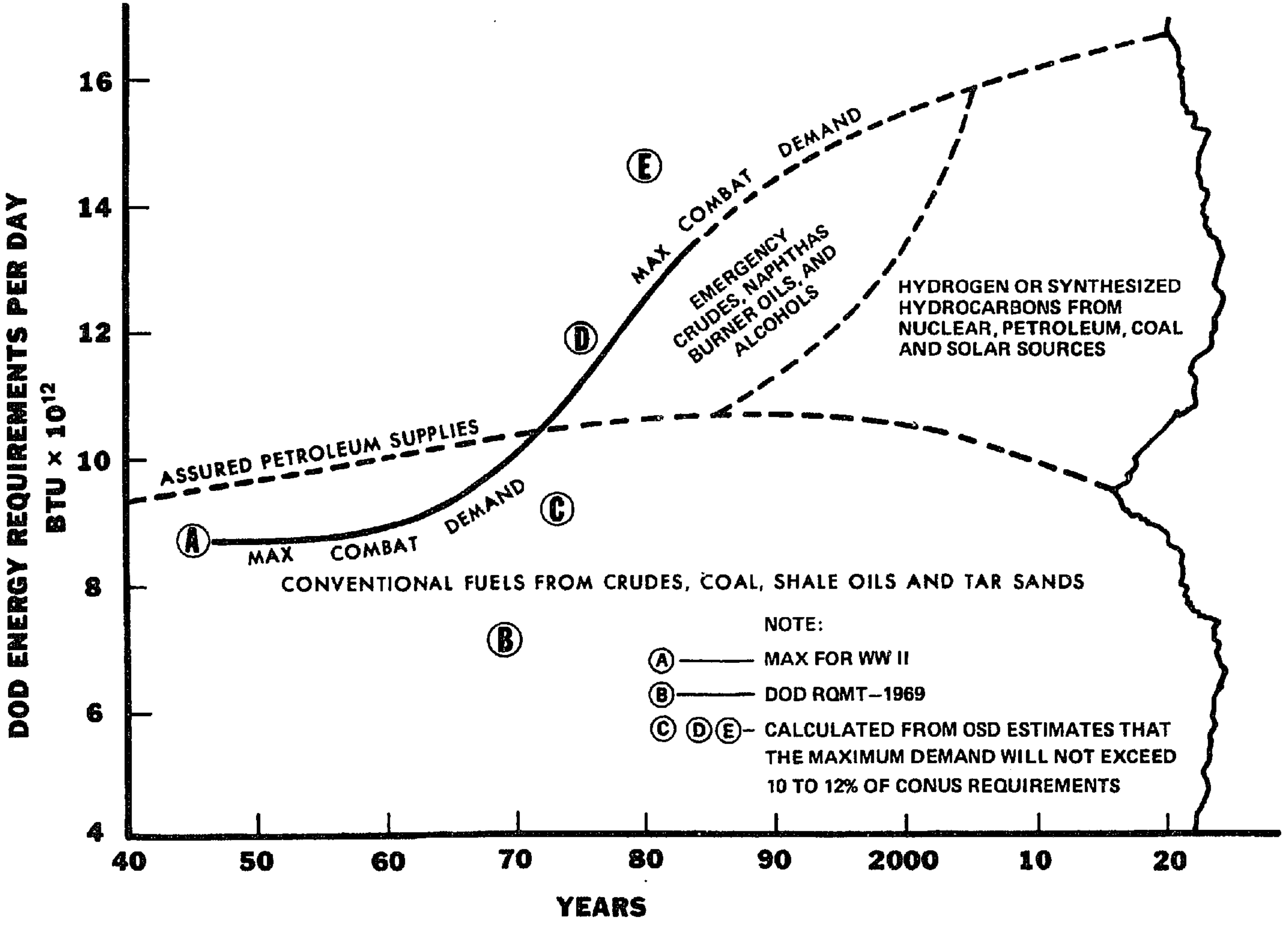
FORMAT

- ***THE FUELS PREFERRED***
- ***THE AVAILABLE FUELS***
- ***ENGINE COMPATIBILITY***

FUEL FRACTION PREFERENCE

FRACTION	CLIMATE TOLERANCE	BTU PER GALLON	FIRE SAFETY	ENGINE APPLICATIONS
LPG	**POOR**	**POOR**	**POOR**	**GOOD**
LT. DISTILLATE	**FAIR**	**FAIR**	**POOR**	**GOOD**
MID. DISTILLATE	**GOOD**	**GOOD**	**GOOD**	**GOOD**
HVY. DISTILLATE	**POOR**	**GOOD**	**GOOD**	**FAIR**
RESIDUALS	**POOR**	**GOOD**	**GOOD**	**POOR**

SUPPLY/DEMAND — COMBAT FUELS



SLIDE 3

CONVENTIONAL FUELS AND POWERPLANTS

	POWERPLANT RATINGS		
FUEL TYPES	GOOD	FAIR	POOR
GASOLINES	**SPARK** **EXTERNAL**	**TURBINE** **STRATIFIED**	**DIESEL**
DIESEL FUELS	**DIESEL** **TURBINE** **STRATIFIED** **EXTERNAL**	—	**SPARK**
JET FUELS	**TURBINE** **DIESEL** **STRATIFIED** **EXTERNAL**	—	**SPARK**

EMERGENCY FUELS AND POWERPLANTS

	POWERPLANT RATINGS		
FUEL TYPES*	GOOD	FAIR	POOR
RESIDUALS	***EXTERNAL***	***DIESEL*** ***STRATIFIED***	***SPARK*** ***TURBINE***
CRUDES (BEST 40%)	—	***EXTERNAL*** ***DIESEL*** ***STRATIFIED***	***SPARK*** ***TURBINE***
DISTILLATES	***EXTERNAL*** ***STRATIFIED***	***DIESEL*** ***TURBINE***	***SPARK***
ALCOHOLS	—	***SPARK*** ***EXTERNAL*** ***TURBINE***	***DIESEL*** ***STRATIFIED***

****LISTED IN ORDER OF PROBABLE AVAILABILITY.***

LONG RANGE FUELS AND POWERPLANTS

FUEL TYPES*	POWERPLANT RATINGS GOOD	 FAIR	 POOR
SYN LIQ HYDROCARBONS	**ALL**	—	—
HYDROGEN/HYDRIDES	**STRATIFIED SPARK EXTERNAL TURBINE**	—	**DIESEL**
HYDRAZINE/UDMH	—	—	**ALL**
AMMONIA	—	**EXTERNAL TURBINE SPARK**	**DIESEL STRATIFIED**
ALCOHOLS	—	**EXTERNAL SPARK TURBINE**	**DIESEL STRATIFIED**

***ALL ARE GOOD FUEL CELL CANDIDATES.**

THE FUTURE OF CATALYSIS

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I wish I were a prophet and could tell you what is going to happen in Catalysis, but I don't pretend to be. I will review some of the many approaches and tools which have been discussed here, and some which have not been discussed should be listed. Then I will discuss briefly some of which we already discussed here, and things that one can readily foresee need to be accomplished, and finally the places at which research can be done. The places at which DOD could help so far as the financing is concerned, and the relative advantages and disadvantages of various places for research will be considered. I have put most of my ideas on slides here.

On the first slide are listed the various tools and approaches that have come to our attention. Under automation I was really thinking of the work that has gradually evolved in surface area work and pore size measurements. In the future, perhaps, you will put a sample in and get the final result all calculated for you. Automation applies not only to measuring surface area and pore size, but to actual carrying-out experiments, and, I am sure, we can look for more and more of this as time goes on. In all probability, we will punch a few buttons and get the experiments done that we want to have done.

Solid State Physics of Surfaces: This includes semi-conductivity work in which our friend, Bill Libby, is an expert and has been very much interested recently. It is not a new field. I reached prominence some twenty-five years ago, and it has been worked on a great deal since that time. I do have the impression that the Solid State Physics work has not really produced many new catalysts yet. Perhaps, the new catalysts are just on the horizon and are about to come forth. But, it is certainly a field to be studied, and one that is of great interest to everybody.

Crystal Field Theory: Dr. Rabo mentioned this in connection with the crystal field inside zeolite materials. The crystal field theory is also being developed extensively now by people like Dowden and others working on the properties of surfaces. The effort is being concentrated on the properties of the surface of crystals, rather than on some of the inside characteristics such as conductivity might lead to.

Spectroscopy has been discussed extensively here. Dr. Peri pointed out the various types include electron spin resonance, and nuclear magnetic resonance.

Single crystal work and the super vacuum work were both illustrated in the talk Dr. Somorjai gave last night. Incidentally, talking about equipment and apparatus, I spend a week each year at Berkeley and I get the impression when I go around from student to student working for Somorjai, that each one is equipped with a $100,000 piece of equipment. So if we were to attempt to duplicate equipment, to use all of the various techniques that I am going to cover here, it would run well into the millions of dollars. The hope is that we can get some kind of cooperation between those who are experts with these various tools, and those who are working on other aspects of chemistry, without any one location necessarily being supplied with all this enormous amount of equipment. In a moment, I have three charts illustrating what I call a Nagle chart. I don't really know where this came from. I was in Europe, in Berlin, France and Spain, and somewhere along the way someone handed me a Nagle chart, and I don't know who it was. It has never been published. Dr. Nagle is at the Naval Research Laboratory, probably Dr. Johnson knows him, and he gave me permission to include this in a publication that is coming out under the auspices of the University of Wisconsin at Milwaukee, Proceedings of The International Surface Science Summer Session. I have taken some excerpts from it to illustrate the types of surface analysis which I think Michel Boudart mentioned here in his talk on the importance of surface analysis. This is a chart illustrating the techniques of surface analysis up to 1972 and from some of the things that Mrs. Libby has been saying here, I suspect there will be a dozen more techniques added to that by this time.

Isotopic Tracers: Keith Hall has covered this very well. We know that isotopic tracer work has been done for some 25 years. I have been very much interested in it myself as is evident from some of the first slides he showed, and I feel very gratified that Joe Hightower and Keith Hall are two dependables that are going to keep carrying on this tracer work because I value it very highly, and I think it can tell us a great many things. So far it has been limited mostly to carbon, deuterium, and tritium. In the near future, it may be extended to include sulfur, because this is a component that we are going to be interested in, and it shows a good possibility of telling us a lot about the detailed mechanisms and confirming some of the hydrodesulfurization mechanisms that were pointed out here in the course of the session.

Finally, I just put down this last item, on Catalytic Theory, and Quantum Interpretation because knowing too little about Quantum Mechanics, I am a great admirer of papers that succinctly make predictions that are useful. I count this paper by Margot from the Shell Laboratory a few years ago on the disproportionation of propylene going into ethylene and 2-butene, as one in which he was able from surface states to preduct the probability that the transition metal oxides and, specifically, molybdenum oxide would be an excellent catalyst. I think his predictions tied in very well with the results of various people, particularly, those at Phillips Laboratory. Another example is the calculation made by Ruch in Germany, in which he calculated that the molecular orbitals of the (111) surface of iron are of such a nature as to fit very well with the molecular orbital of nitrogen molecules, and therefore, he predicted that the nitrogen molecules would adsorb on the (111) face of iron in preference to the (100) and (110) faces. Now this is exactly what the LEED people find, that nitogen is chemisorbed on the (111) face, rather than on the (100) and (110) faces. There has been an erroneous conclusion from this that nitrogen molecules are involved as intermediates in the ammonia synthesis and this is a long story in itself, but, nevertheless, it is a second illustration of a calculation of an interaction of gas molecules on the surfaces, and it looks very reasonable. I notice in the August Journal of Catalysis, that there is an article on the calculation of surface states in connection with adsorption. So I think this field is coming more and more into prominence, and in the near future, I will certainly look forward to the probability that theoretical assays can be made of surfaces, with some very fair predictions that will be important to practical work, as well as, to basic work. So this is an outline of a few of the tools and approaches that have come into existence and seem likely to be of continuing importance.

The next three slides all refer to the Nagle chart (see appendix B). I have used initials only when they are obvious; don't ask me to explain all of these. The spectroscopy is quite clear. The nuclear magnetic resonance, electron, spin resonance, ellipsometry, emission spectroscopy, field desorption, ultraviolet emission, X-ray fluorescence, and appearance potential spectroscopy.

These are all the result of plotting various types of radiation that could be imposed, including infrared, ultra-violet, visible and gamma rays, and finally electrons, positive ions and so forth, against the quantity to be measured, and at the intersection of each of these comes out one of these new techniques. Mössbauer spectroscopy particularly, we have had described in great detail for its effectiveness. Incidentally, in line with the chronology that you mentioned, I recall that in September 1963, I reviewed for NSF the first paper that had come to my attention on the use of Mössbauer spectroscopy to study the surface of iron synthetic-ammonia catalysts. I think it was one Harold Low was presenting. But, that fits in with your statement that about ten years ago Mössbauer spectroscopy got under way. You recognize Auger spectroscopy and mass spectroscopy. Most of the techniques I am mentioning here are fairly new. Mass spectroscopy is, of course, an old timer.

The LEED work we know, and is so beautifully illustrated by the results that Dr. Somorjai was reporting yesterday. This sums up to 25 tools designated as surface analysis methods and summarized in this chart by Dr. Nagle.

I would like to draw the conclusion that the basic study of catalysis must be a very interdisciplinary procedure, such as various people have pointed out here in the course of the meeting. This is well recognized, and the greater the amount of interdisciplinary cooperation that can be brought into catalysis research the greater the progress that we can make in understanding how catalysts work.

The next slide summarizes some of the problems we have been talking about. I stole most of them from the program. It is obvious that taking the lead out of the fuel requires alterations to be made in petroleum technology to produce the necessary octane to run our automobiles. This is a rather obvious change that is going to demand catalytic attention. Fuel from unconventional sources, shale oil, and various other sources, has been pretty well covered, as well as, auto exhaust and desulfurization. As I understand, it is the government that is finally moving on desulfurization, at least I think there are plans to push the hydrodesulfurization work and we may see quite a bit accomplished in that in the near future.

Catalysis in closed cycle hydrogen production - complex cyclic processes to produce hydrogen chemically. The very simplest one that occurs to me immediately is to simply decompose water vapor over a catalyst at, let's say 700 degrees Centigrade. One <u>can</u> decompose water into hydrogen and oxygen at about 10^{-7} mole fraction of hydrogen. Now if one wants to separate out the water, separate the hydrogen from the oxygen, and compress the hydrogen up, one can wind up with hydrogen at one atmosphere produced from water vapor. One can also arrange chemical processes such that by carrying out four or five reactions in series, at very different temperatures, in between steps one may have some concentrating or some evaporating to do. One winds up producing hydrogen from water as a sole reactant. I think I have seen at least 10 of these reaction schemes. I didn't bother to put any of them on a slide, but there were some listed in the Industrial Engineering Chemistry News recently. But nobody so far as I know has mentioned any catalysts in connection with these. If any of those cycles work, it is almost certain that some of the cycles will have to be catalysed and this is why I include the closed cycle hydrogen production as a possibility in the future.

Fuel cells we just heard about are important for pollution control; such as catalytic processes for stack gases and various other aspects of pollution control.

Not much has been said about homogeneous catalysis. There were several homogeneous catalyst experts who were invited for this meeting, whom I hoped would be here, including Halpern and Coleman, but I don't believe either one is here. Homogeneous catalysis has become very important, and I like to look on it particularly as sort of connecting link or bridge between heterogeneous catalysis and enzymes, which are so important. I might digress to say that when I came to the Fixed Nitrogen Lab in 1926, Dr. Cottrell was director, and he tried very hard to get Dean Burk, who was a biochemist there working on nitrogen fixation by azotobacter, and myself working on iron synthetic ammonia catalysis to collaborate and exchange our ideas. Well it just didn't work somehow. They are so far apart that you review each other's papers and try to listen to each other's talks, but never achieve any very intimate relationship. So heterogeneous catalysis and enzymes have stayed far apart, but I do see that homogeneous catalysis stands a chance of bridging the gap. People have even talked about synthetic enzymes made by putting well known homogeneous complexes on certain types of surfaces.

The last item I mentioned here is <u>pore size quantization</u>. If one reflects a little bit on some of the things that have been said it is quite apparent that pore size control for different catalysts is very, very important and we're only at the start of being able to quantize the requirements of pore size. We know how to get pores of different sizes. We need to be able to quantize them, not only into absolute sizes, but into distributions. Sometimes, we want a combination of big pores and small pores, and I think pore size quantization probably has quite a way to go.

Well, these are a few of the fields that suggest themselves as a result of what we discussed here.

The rest of the time, I would like to devote to talking about places where catalytic research can be done. I think I have listed all of them here. <u>University Research</u> includes catalysis being done in universities. I recently had occasion to count articles over the last nine months of the Journal of Catalysis. The first surprise that came out was that between 60 and 70 percent are foreign articles, which disabuses us of the idea that this is a publication of American work. In each issue there are on the average, about ten basic articles from the universities and industry, divided about equally. So the university research is certainly one place in which basic research is being done.

I have one or two comments on university research. Naturally, I am for it and I think DOD should support all worthwhile university research that they can spare funds for, because this is a place in which at the moment there is an interest in basic research, and inwhich there are more or less good facilities, not the $100,000 variety, but nevertheless facilities for doing basic research.

There is one thing that was impressed on me recently, that maybe some of you can do something about. There is a human mortality to university research. I am thinking particularly of Atkin's work at University of Wisconsin, at Madison. He had an extensive program going on in organic catalysis, and when he died the program so far as I know was dropped. I thought I was fixing things up nicely, you see, at Johns Hopkins by having a reliable person, Dick Kokes, to take my place; but his untimely death last July 27th left his catalyst group floundering, and I suspect that it is going to vanish. At any rate, most University research is a one man proposition, and I'll leave it to you to figure out for yourself which are one man catalyst programs. I know of a few examples of groups that have more than one senior faculty member. I think there are at least two, maybe three, people at Berkeley. Cal Tech has several people. Certainly the University of Wisconsin in Milwaukee, where Keith Hall is going, has quite a number, but these are the exceptions. The general rule is that the University research programs, such as have been built up at Johns Hopkins, Princeton, and various places, are one man programs, so this is a weakness we just have to keep in mind. Maybe those of you that are in sole charge of such research, can have a standby to fall back on, but I am dismayed at the way in which the passing of an individual can result in research in universities being discontinued so far as catalysis is concerned.

Industrial research I have little to say about except that it publishes half the fundamental papers and I am calling fundamental papers here, those that are published in Journal of Catalysis. You could argue over the definitions; some of them are along practical lines but I took all of them as being basic papers and half of them are in industrial research. I think those of you who are in industry recognize the fact that industrial research rises and falls depending on the period of economy so far as basic work is concerned. When the economy gets in a bind very often the powers-that-be cut down on the basic work and limit one to applied work. But over the years a great deal of very fine work has come out of industry. One has to think only of Val Haensel here with his platforming catalyst to realize what beautiful results can flow from industrial research laboratories.

The present institutes are going to be discussed this afternoon. Of the present institutes, my recollection and impression is that they have had their ups and downs, sometimes more downs than ups, but Dr. Wise is here and can tell the details as to how one very prominent institute has fared. I don't really know the magnitude of the work going on there, but certainly it is a portion only of the total work of the institute. It is a good place for work to be done and certainly should be financed.

Government Research Projects: I am thinking particularly about the National Laboratories. At Oak Ridge where I have been a consultant for a good many years, there has been catalytic work on the effect of radiation on catalysts, but nothing very extensive. They are thinking now of new projects so there may be an increase in the amount of good research in catalysis at the Oak Ridge Laboratories. I am not too well acquainted with the other national laboratories, but I don't believe there is much catalysis in any of them. There was some at Brookhaven at one time, but I haven't heard much of it for a number of years.

Bureau Research: Here I am thinking of the Bureau of mines, Department of Agriculture and so forth. I was in the Fixed Nitrogen Research Lab during a period in which it was sort of a paradise so far as basic research is concerned. There were about nine project leaders, including Sterling Hendricks, whom you all know for his x-ray work. I was in charge of catalysis and we were free literally to do just about anything we wanted in the way of research.

At a certain point John Turkevich, Alex Oblad, and I strongly recommended, in a report funded by the AFOSR, to establish a National Catalyst Institute of some 50 senior research people.

Nothing was ever done to implement it. This is an area to which very serious consideration ought to be given because many of the things we mentioned here such as a bank for catalyst samples, interdisciplinary types of information, and so forth, all of these could very logically come out of a catalytic institute. The idea that we had in mind, at the time, and even now, is a basic building unit consisting of perhaps 50 scientists in different fields, including people who could reasonably work in together with honest to goodness catalysts. For example, we've needed catalytic people that are doing actual practical catalytic work, because the object of all this would be to bring them and all their ideas together with those who are interested in more basic approaches to the study of certain aspects of catalysis. So, it would be an opportunity for an inter-disciplinary approach. The institute should be located on a university campus in corroboration with a university. Now, there are lots of models for this, but I like to think of the one that the University of Iowa has as being a very satisfactory one. The more you can intermix the faculty of this institute with the faculty from the university, the fewer problems you will have. There will always be the question of whether you're stealing graduate students from the chemistry department or the physics department, for working in your institute. One of its functions should be to train young students and encourage them in the field of catalysis, and this could be done by letting them do their research work in the institute and of course have all of the course work, or most of it, done in regular university circles. The experience of the last ten years has reinforced my conviction that a national catalytic institute acting as a back bone for supporting basic catalytic research in assuring continuity of effort is even more desirable now than it was ten years ago. I wouldn't want it in the least to diminish the support given to these other various sources; all of these various groups that I've mentioned here should be supported. But, the coordinating action of a national catalytic institute would be helpful. And, as John Peri pointed out a while ago, if some of these various things are implemented and we can get research funds for carrying on, the future of catalysis should be rather bright. Now, I'm stopping ten minutes early; are there any questions that anyone has?

Discussion

W. F. Libby: Paul, if you could write the national budget for catalytic research, what would be the number?

Emmett: Ten years ago, we were looking for a Santa Claus who had $50 million. This would have included about $5 to $7 million in building and equipment. I'm not sure what the present costs would be, but a modest installation of equipment and a building could probably be built today for $10 million. For that size group ten years ago, the figure $1.5 to $2 million was adequate to cover running costs. Perhaps, the modern figures should go up to $3 million a year.

So, if one were looking for a Santa Claus, instead of $50 million, somewhere in the range of $75 to $100 million would be necessary. Now, for practical reasons, one needs a source for getting the building and equipment going and one might get support by a variety of ways. The chief thing would be to detach it from political strings so that changes in politics wouldn't subject it to year to year fluctuations; it would have continuity. Dr. Bloch at the Fritz-Haber Institute in Berling said that the Berlin government has taken over his institute. It used to be divided between industry and government, but now it's a sort of a sacred charge with government providing close to 90-95 percent of their budget, continuously so long as the country lasts. So they don't have to worry and they proceed merrily with some very nice basic work.

Hall: I put some information together for the National Science Foundation for release appropriate to mention here. At Gulf Research the budget for total research in catalysis has increased continuously over the past period of 5 years. But the support for basic research, although difficult to define, has decreased from about 41% to 14% of the total budget for catalyst work. These calculations were made in a consistant way and were little affected by closing out the effort at the Mellon Institute. In defining "basic research" everything that could remotely be assigned to this category was included, whether it was tied to an applied project or not. If these data are typical of industry as a whole, and I think this is probably so, it is clear that industry is spending somewhat more money for applied research, and considerably less in the basic areas. When trends in other nations such as Japan and the USSR are considered, this is a little scarey.

Voice: Constant dollars, or not?

Hall: Constant dollars.

Emmett: Somebody from Oak Ridge who was asked on Friday night to have ready by Monday morning, figures for the total amount of money being spent in basic catalyst research. I suggested whom he should call and he got an estimate. We checked up in various other ways and it looks as though 12 to 15 million per year would represent a fairly good guess of the support of basic research in industry, government, and the universities.

Haensel: That's terribly low, Paul.

Emmett: You think that's low? Well, I told them to call you, but I don't think they did. The highest estimate we got was $15 million. So, it could be low. Certainly, adding surface and enzyme research, it comes to about $30 million.

Haensel: The problem there, Paul, is the definition, how basic is basic?

Emmett: This is right.

Haensel: Now, if we consider whatever basic work we do in conjunction with an applied project, it is still basic. And it becomes confused, it becomes a matter of semantics.

Hightower: The percentage of papers authored by industrial people in Journal of Catalysis over the last eleven years has dropped by a factor of two, exactly.

Emmett: That's interesting.

Mills: You just mentioned that of the new scientific projects to be supported by the government the one that stands out strongly is the $10 billion five-year energy program for which Dixie Lee Ray has on December first to make a recommendation. Obviously, from some of the discussions here, especially on non-conventional sources, part of this is for basic research. If we are going to be successful in the energy program, it has got to be backed up by catalytic research.

Emmett: To ease your mind, Dixie Lee has been given recommendations for the National Catalyst Laboratory.

Voice: December first is when the recommendation will be made.

Emmett: Yes, a recommendation has already been submitted to her on behalf of basic research.

Ruby: I might mention that with Leona's help we have put in a bid for a Catalysis Institute. Unfortunately, the Director of Research, the Director of ARPA, thought it was not suitable for support by ARPA alone.

Emmett: It is being proposed from at least one other point of view, but perhaps I shouldn't talk with the recorder going.

Voice: The formation of institutes is progressing very rapidly. There is recently a pipeline institute and a railroad institute serving the campus of I.I.T. I would say your cause would be helped tremendously to get government support if you could show a payoff for the investment, becaust that is the way we fund these things.

Lindquist: One of the problems that's facing basic research in industry is the devastating effect on the Department of Defense study by M.I.T. of the effectiveness of basic research. There was a report that came out about four or five years ago that said basically to forget it for 20 or 30 years. That has had a devastating effect especially on the energy crunch that we are facing now. It is hard to sell basic research that pays off 20 years from now, when the problem is the next three to five years.

Emmett: I would like to consider that as one man's opinion. I suspect that that is what it does boil down to, but unfortunately it does reach quite a number of sources.

Boudart: The Nagel table which was never published by Nagel, has been published by Rhodin and it is available in the Proceedings of the National Symposium on the Reactivity of Solids that was held in Bristol in 1972.

Burwell: The Nagel table with its spectrum of techniques is not as useful as may appear at first sight. A great many of the techniques on the Nagel list cannot, in any simple way, be applied to analyze catalysts of practical interest. For the analysis of platinum, any technique that doesn't detect a tenth of a percent of a total monolayer is essentially useless, and that's a minimum. Furthermore, most of the platinum particles are inside of silica granules. Any chemical physics technique that requires ultra high vacuum is in difficulty. These techniques are used in surface analytical chemical physics and eventually they will be applied to catalysis. But, most of them cannot be applied in catalytic work at this stage. Further, some of them are destructive to many kinds of chemisorbed species. But they have serious problems and as Professor Boudart points out, you don't just run an experiment and immediately get a meaningful answer. In time one will, but not immediately and not easily.

SPECIAL APPLICATIONS OF CATALYSIS IN FUEL CELLS

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What I say does not represent an official Army or DOD position. We've heard requests of "Let's hear from DOD," throughout this meeting; however, DOD does not speak with a single voice, but rather with numerous voices in matters such as the one under discussion. For example, I belong to the Electrochemical Working Group of the Interagency Power Group and it takes us two days, once a year, to go through and briefly discuss all the battery and fuel cell programs handled by the agencies of DoD. I'd like to cover our one tiny facet; I'm Chief of the Electrochemical Division, which consists of 28 people, in the Electrotechnology Department, which has 150, at the Mobility Equipment R&D Center which numbers about 1350 people, total. Our responsibility in this one small department covers mobile, non-propulsive, power plants with power ranges from 0.5 - 200 kilowatts. We aim for all these power plants to have reliability, availability, and maintainability, the acronym for which is RAM. The fuel cellsthat we work on are for the 0.5 - 5 kilowatt range. Catalysis comes in, in many ways. Our task is to operate these fuel cells on logistically available fuels. Our specs say that our fuels can have up to 4000 parts per million sulfur which is larger than in most fuels available in this country, most of which are down around 2 or 3 hundred parts per million. The fuel cell systems that are most advanced are, of course, indirect. This slide shows a fuel cell operating on a mode of fuel conversion, namely, thermal-catalytic cracking, chosen to fit the RAM criteria. It's a simple system, and fairly reliable. It does not require water, as reforming does or partial oxidation, so we don't have to worry about transport of water in the field. One of our major problems is that for this

Huff (Continued)

mode of fuel conversion, there's no commercial base technology, or none at least that we've been able to find.

Haensel: We've had 30 years experience in thermal catalytic cracking.

Huff: But not in miniature systems, this is our problem, Dr. Haensel, producing only hydrogen and carbon. Methane is an impurity for us, which we'd like to keep as low as possible, as is also carbon monoxide, which fuel cell catalysts do not like. Our systems, at the moment, give us 95% hydrogen in the fuel feed to the cell. Since there is no commercial base, and this applies also to the engines that we've built, the cost becomes excessive. We're trying for a life of about 1500 hours. We're using a dual column type system, where we generate in one and burn out in the other at the same time, with fairly reasonable heat transfer and conservation. We operate between about 1400°F and 1600° to 1700°F. The switching time is about 4-1/2 minutes. Our other problem is to attempt to burn these fuels directly. In addition to Dr. Haensel's two ways of modifying catalysis either internally or externally, in electrocatalysis we can also apply the potential to the surface and we also have the effects of the electrolyte solution, for a total of four modes. Incidentally, Dr. Emmett omitted us from his list of laboratories that are doing catalytic research. It may be that we don't advertise enough. This slide lists the techniques that we are currently using. The first one is strictly an electrochemical technique combined with gas chromatography. We're doing all of these in-house, except, the carbon-13 labeled work, which is being done at State University of New York at Buffalo by Dr. Bruckenstein. We've been in the hydrocarbon oxidation mechanism business for about 10 years. Probably the other reason we didn't qualify for Dr. Emmett's list is because of the mixture of people I've got who like to publish in J. Organic Chem. or J. Phys. Chem. on occasion, but don't publish in the Journal of Catalysis. So, unfortunately, they don't get included. We're quite enthused, and we just talked about it in an Electrochemical Society meeting, about changing the electrolyte solution. We're troubled very greatly by surface poisoning as we run even simple hydrocarbons. This poisoning effect will kill a fuel cell platinum electrode in about 140 hours. We get low voltages from these systems. We've changed the electrolyte solution from phosphoric acid that we've worked in most of the time to a trifluoromethane sulfonic acid monohydrate and in initial tests on a platinum wire, we've found 1,000% increases in propane oxidation. We're very enthused and think this is a good possible way to go. Two other firms that we deal with in the fuel cell business are Engelhard and Energy Research Corporation. Joe mentioned that he'd like an informal comment on hydrogen generation from the hydrogen economy people, and I have become involved in these efforts too. The thermal processes that Dr. Emmett mentioned are not catalytic so far as I know. A main portion of this work has been carried out in Europe by DeBeni and his co-workers at EurAtom in Italy. They are through process Mark-9 now, and that one consists of 8 or 9 different steps the second of which generates hydrogen. The later steps are for the purpose of trying to get back to the starting materials. It has materials problems just as a high-temperature fuel cell has materials problems. The other place where a significant impact can be made in the catalysis business is in electrolizers operating with a nuclear power plant sitting in the middle of the ocean. The most recent technology being used is a fuel cell technology that dates back to about 1966. We've made considerable progress in both catalysts and electrodes since then, in rather a major effort. It's a difficult system, with gas being evolved at a very high rate, but if you can save even a tenth

Huff (Continued)

of a volt or two tenths of a volt, the process can become economically viable. At the same time, a lot of free oxygen is being produced which could be processed in other catalytic systems or used for waste treatment or whatever use you might want to find for it. Thank you.

CATALYSIS RESEARCH IN RESEARCH INSTITUTIONS

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At this stage of our deliberations, I'm reminded of the predicament in which a new member of Parliament found himself, when he asked Disraeli whether he should participate in the discussion taking place in the House of Commons at that time. Disraeli very quickly sized up the situation and decided,"No, I think not. It may be better for people to wonder why you didn't speak rather than why you did." Actually, the topic of my talk and the framework in which we are discussing catalysis, tempt me to play the devil's advocate. We are here not only to discuss catalysis but specifically the role of catalysis in the needs of the Department of Defense. The question to be asked is: How should the system of scientific choice be institutionalized? In other words, where is it best and most expedient to do research in catalysis to serve the needs of the DOD?

Now, the state of the art is best summarized, as far as heterogeneous catalysis is concerned, in some quotations from four gentlemen, two of whom attended this meeting but decided to leave early. One is Dr. Heinemann[1], who said in 1960 at the Catalysis Congress in Paris: "For at least the past 70 years, all discoveries in applied catalysis which have opened up new fields of industrial importance, have been based on empirical work rather than deductions from basic understanding," followed by Professor Taylor[2],

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[1] H. Heinemann, Second Internat. Cong. Catalysis, Technip, Paris 1960, Vol. I, p. 129.

[2] H. S. Taylor, Adv. in Catalysis, Academic Press, N.Y., 1957, Vol. IX.

who at that same congress, commented. "It is a marked characteristic of the catalytic development, that the empirical art has always been in advance of the science," and Professor Emmett[3] who added, "Catalysis has been correctly designed as an art. Within the last 30 years the art has gradually been acquiring a considerable coating of scientific lustre." That was in 1960. In 1964, Professor Nyholm[4], offered the following comments at the Congress of Catalysis in Amsterdam. He said: "In reading papers on catalysis, one is struck by the following main features which I suspect have influenced my approach to this subject: First, the wealth of unexplained empirical experimental data which are already available; secondly, the frequency with which explanations have been advanced which seem, on closer examination to involve little more than giving the problem a new name; thirdly, in spite of the wealth of kinetic data available, the great need to discuss the catalytic behavior in heterogeneous catalysis in terms of the properties of individual atoms." Now, I'm inclined to believe that these comments made in 1960 - 1964, apply equally as much today.

Since the preceding lectures have dealt with some of the problems facing heterogeneous catalysis, it is rather striking that the significant developments in catalysis during the last 30 years have been in the areas of Zeolite catalysis, reforming and platforming, olefin oxidation and ammoxidation, ethylene polymerization, hydrodesulfurization, ammonia synthesis, and methanation catalysis. Except possibly for methanation catalysis,

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[3] P. H. Emmett, Catalysis, Reinhold Publ. Co., New York, 1954, Vol. I.

[4] R. S. Nyholm, Third Internat. Cong. Catalysis, J. Wiley & Sons, N.Y. 1965, Vol. 1, p. 25.

which uses still the same catalyst that Sabatier[5] described in 1902, nickel catalyst, all of these major developments originated in industrial laboratories. Now, why is that the case? Probably the major reason is the fact that catalysis is not a discipline. It takes a group of people representing a spectrum of scientific talents, different disciplines, including, inorganic structural chemistry, organic chemistry, surface chemistry, spectroscopy, solid-state physics, mass and heat transfer and so on, to try to understand the functions of a catalyst. In many of our fine industrial laboratories, such an array of scientists is assembled. Perhaps their multi-disciplinary approach explains their success. I understand that 25% of all the manufactured products in the world today have a catalytic process someplace in their manufacture. That's a staggering thought! As a matter of fact, I understand from our economists at the SRI that 80% of all petro-chemical products are produced catalytically.

This coupling between the disciplines which seems to be the key factor, exists in industrial laboratories and is a factor of which we should certainly be aware.

The various laboratories can be classified in terms of motivation for the research. First we have product oriented research laboratories where there is a vertically integrated organization, capable of producing a process from the stage of research to development and manufacture, but whose scientific activities serve another purpose. Their motivation is to develop

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[5] P. Sabatier and J. B. Sendereus, Compt. rend. 134, 514 (1902).

a product and a financial profit. Secondly, the academic oriented research institutions, which, as was described by Prof. Emmett, are narrow but intensive in their approach to catalysis. They often revolve around single individuals. Coming from the University of Chicago, I would like to quote a comment made by Robert Maynard Hutchins who said: "Let us not forget that a university is composed of university professors, a group of individuals held together by a central heating system." Finally, we have the technical mission-oriented laboratories, research establishments with technically defined missions. This may be high energy physics, micro biology, catalysis, and so forth, and this is a category to which many of our research institutes belong. I must admit that there is a spectrum of research institutes: the endowed research institutes, the nonprofit research institutes, the not-for-profit research institutes, and I guess a few bankrupt research institutes as well. These institutes represent a mission-oriented research effort whose goals change from time to time because they are governed by a triangular interface, consisting of the government on one side, industry on the second, and fundamental research on the third side. It's this interface which interacts at a research institute, allows it to function, and to help in the solution of problems of government and industry. The R&D problems faced by the DoD fall predominantly into this category. But some service can be rendered by all three types of organizations I mentioned; the product oriented research institute, the academic oriented research institute, and the mission oriented research institute.

4.

If I may make another quotation, the DoD faces a problem very similar to that of Rolls-Royce when Sir Denning Pearson, the president, pointed out that, "building a new engine will not guarantee that we stay in business... not building one would certainly guarantee that we are out of business." The problems in which DoD should have an interest, far surpass those that we have talked about at this meeting. They are not only the problems facing the petroleum industry. The DoD's problems span a range including (1) non-fossil fuel technology involving hydrogen and hydrogen carriers as fuels, (2) coal-based technology, (3) solid-propellant catalysis, (4) liquid-propellant catalysis (current problems associated with liquid propellant catalysis deal for example with such areas as the endothermic catalytic control of the hypersonic aircraft, thruster control in outer space by our satellites involving hydrazine as a monopropellant with iridium as a catalyst), (5) catalytic long term life support systems, (6) electro-catalysis, (7) photo-catalysis, (8) nitrogen fixation, and (9) catalysis at plasma boundaries (as occurs in high intensity lasers). These are some of the problems that have been DoD sponsored and in which catalysis has played an important role. So, I would like to suggest that one should not ask whether DoD should participate in the support of catalytic research - they are doing so already. Rather one should ask where they should place their support for catalytic research.

Thank you.

Discussion:

MacCormack: Relating to the motivation in work on solid propellant catalysis, one area the Department of Defense is very interested in is explosives, which generally are modified by changes in chemical structure or by putting in materials acting as heat sinks. It's somewhat difficult to conceive of catalysts which will change a chemical process faster than a detonation wave goes through it. But you could consider such things as putting in bonding sites that would coordinate with nitro or amino groups thereby modifying the chemical preenergy behavior as a concommitant to the chemical structure of nitro bodies.

What other roads are there to catalysis in explosive systems? I don't really know enough about the field to make any further commentary.

Hightower: Is there anyone from the DOD who would care to address himself to that question, that issue? Any further questions? Thank you.

ACTIVITIES OF THE CATALYSIS SOCIETY

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What I have to say is an official statement of The Catalysis Society, although it is not at all clear what that means. There are about 1400 members of The Catalysis Society and if you want to get in, there are two ways you can do it. Either you join one of the Catalysis Clubs or you can join directly for some quite large fee, I think it's a dollar a year. But since the number of direct members is so small it is immediately obvious that really The Catalysis Society is the sum of the clubs. I should immediately point out for the benefit of the DOD representatives that it is not an American institution; it's a North American institution. It covers both the United States and Canada. Perhaps, a short history might help in making this mysterious organization look reasonable. It started about 1950 in Philadelphia when a group of people organized the Philadelphia Catalysis Club. This was so successful that Chicago, always anxious to be, if not first, the second city, started a Catalysis Club. Now the Philadelphians were very energetic and they got the idea of an International Congress on Catalysis. One had never been held, they organized it and asked Chicago to cosponsor it. Chicago did, but the Philadelphia Club did almost all the work. In 1956, the First International Congress on Catalysis was held in Philadelphia, and was so successful that there was a universal demand for its continuation and the meeting organized itself to continue. The French offered to field the next one which was arranged for Paris in 1960. But the First Congress had left a small profit. This required certain activities, including incorporation, and so there was now incorporated the International Congress on Catalysis which, like the World Series, had a purely American Board of Directors, and which then was presumably a holding organization. At the Paris meeting, some of the other countries, the Russians particularly, objected to the International Congress on Catalysis having a strictly American Board of Directors. So in 1964 in Amsterdam, there was set up a new International Congress on Catalysis with an appropriate international Board of Directors. This, then, required the dissolution of the old International Congress on Catalysis and The Catalysis Society was incorporated to take its place. It serves as a service agency to the various Catalysis Clubs which have grown over the years. There are now, in addition to the Philadelphia and Chicago Clubs, Catalysis Clubs in New England, New York (which includes Northern New Jersey where most of its members live), Pittsburgh, the Southwest, California, and the Canadian Catalysis Club, which has a somewhat different name and is a subdivision of the Chemical Institute of Canada. Each one of these elects a member of the board and there are currently three elected at large. The functions of The Catalysis Society are as follows: it sponsored and ran the Fifth International Congress on Catalysis which was held summer a year ago, it issues a newsletter, it has a bi-annual meeting, the next of which will be in San Francisco in February, it provides a national lecturer, who has so far always been a European, and who visits the various Catalysis Clubs giving what is now called the Ciapetta Lectures, named in honor of a deceased member who contributed greatly to The Catalysis Society. And, that, I think, is about the sum of what it does. It is a scientific society, with no professional activities. It does exemplify one rather curious sociological feature which may be worth noting. Its members include both academic and industrial chemists and both chemists and chemical engineers. There are probably few areas of the physical sciences in which we find sitting together conversing so frequently both an academic man like, let us say, Professor Boudart, and an industrial man like Dr. Peri.

Discussion:

Hightower: Thank you.

Haensel: Bob, you did not mention a very important output of the Congresses, and those are the volumes like the one that Joe Hightower edited last year.

Burwell: Congresses have volumes and we have our two handsome volumes in which it is incorrectly stated where the Congress was held.

Hightower: Everything's accurate but the title page, Bob. Any other questions or comments? I think The Catalysis Society certainly does play a very important role within the catalysis community.

RESEARCH IN CATALYSIS AT THE BUREAU OF MINES

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Twin Cities, Minnesota 55111
(612) 725-4634

About two years ago, to be exact on May 20, 1971, I had the privilege of participating in a two-day symposium at the Lawrence Radiation Laboratory, University of California at Berkeley. The meeting was chaired by Professor Bert Meyer, and the culprit was SO_2 whose abatement chemistry and technology was of top priority in those days of environmental concern. Representatives of EPA were present to evaluate and compare between lime scrubbing, aqueous or dry, catalytic conversion, oxidation or reduction, throwaway processes, Thames water or sea water, etc. Among many other SO_2 abatement methods was one being developed by the late D'Arcy George and Dr. J.B. Rosenbaum at the Salt Lake Metallurgy Research Center. The method uses a buffer solution of citric acid-sodium citrate of pH 3.5 to scrub SO_2 from the gas stream. When this procedure was mentioned in one of the discussion periods, Professor Thomas Sherwood (who steered the program) exclaimed, "If this method succeeds, they've got it licked". I am pleased to report now that the Bureau of Mines citrate process is in the pilot plant stage. More about the citrate process after a brief description of the energy problem in the resources framework.

In a global sense, for the existing species of mankind, the "energy capital" was produced millions of years ago by the storage of solar energy in the form of chemical energy through living organisms. This energy is stored in fossil fuels, coal, gas, and oil, and only lately man began to realize the finiteness of these fuels in the sense that they are depletable. For his survival, man must therefore adapt himself to the concept of "energy income", the resources of which are continuously replenished, either instantaneously by direct use of solar energy or after a short period of storage in the form of winds, rivers, natural steam, or biomasses such as wood, animal waste, plant leaves, etc.

The distinction between an income or a capital of energy depends on its storage time scale. Because we are going to depend more and more on energy income, we must think of reducing the millions of years of storage to months or weeks of storage, or perhaps to instantaneous or direct energy conversion. Catalysis is the art and science of accelerating change, hence the decision by DOD and ARPA to attempt resolving some aspects of that important shift in energy from capital to income by research in catalysis is indeed a wise one.

One of the major catalysis programs in the Federal Bureau of Mines involves the coal gasification reactions, and these were ably covered yesterday by Dr. Alex Mills. The Bureau of Mines divides its research activity among three sections, Energy research, Mining research and Metallurgy research. Dr. Mills is a chief in energy research, I work in metallurgy research and hence my statements will be confined to the latter.

Before discussing catalysis in metallurgy research, let me add one last satirical point. The national call for "energy conservation" appears to be somewhat inexact since energy is conserved anyway in obedience with the first law of thermodynamics. A more exact call should perhaps be to "lower energy dissipation" or to "suppress our entropy vector" so that mankind can survive longer, especially when energy and matter are taken together. If the word conservation is desired, then we should attempt to conserve fuels.

In recent years, the Bureau of Mines has studied a number of methods for conserving premium grade fuels used in the mineral processing and metal producing industries by the substitution and alternative use of lower grade and lower value fuels. Projects at the Twin Cities Metallurgy Research Center are being oriented towards the feasibility of reducing iron oxide pellets with solid fuels rather than the currently used natural gas, and the reduction by roasting and possible metallization of iron oxide pellets with low-value fuels which can also function as reductants.

Since we are going to dig into the vast reserves of high sulfur coals, viable methods of SO_2 emission control become imminent. Catalytic reduction methods appear to be attractive, but they suffer from the presence of O_2 and/or water vapor in the flue gas. Mr. L. A. Hass and I have published a number of articles in the Journal of Catalysis on the catalytic reduction of SO_2 to elemental sulfur on an iron alumina bifunctional catalyst. Although the presence of water vapor can be coped with by the inclusion of a post Claus catalyst of pure alumina, the presence of O_2 is detrimental because it increases the stoichiometric proportions of CO needed to cope with both SO_2 and O_2. By contrast, the citrate process does not suffer from these limitations. In brief, the citrate process is a three-stage process as shown in the flow diagram of the following slide. Gas cleaning, cooling and absorption in an aqueous solution of partially neutralized citric acid comprise the first stage. Production of high purity elemental sulfur by reaction of the loaded solution with H_2S gas occurs in the second stage. The third stage involves the production of the needed H_2S by reacting two-thirds of the sulfur produced in the second stage with methane and steam. Reactions in the second and third stages of the citrate process can be greatly enhanced by catalysis.

Another important research area in the Bureau of Mines involves energy conversion schemes. Direct isothermal conversion of chemical energy due to oxidation of a fuel into electrical energy is thermodynamically more efficient than the indirect heat or mechanical engine path. The Carnot efficiency limitation inherent in the conventional thermoelectric plant does not interfere with the fuel cell device. However, the latter requires a catalyst, invariably platinum which is not abundant in the U. S. A research project at the Reno Metallurgy Research Center deals with the investigation and utilization of the catalytic properties of rare-earth elements and their compounds. Similar to the partially filled d-orbitals in transition metals, the partially filled f-orbitals in lanthanides should endow them with catalytic activities. Electrodes are important components in fuel batteries, hence the research at Reno is also directed to develop electro-conductive catalytic materials for application in H_2-0_2 fuel cells. It must be admitted that the theory of electrocatalytic processes is still in its infancy.

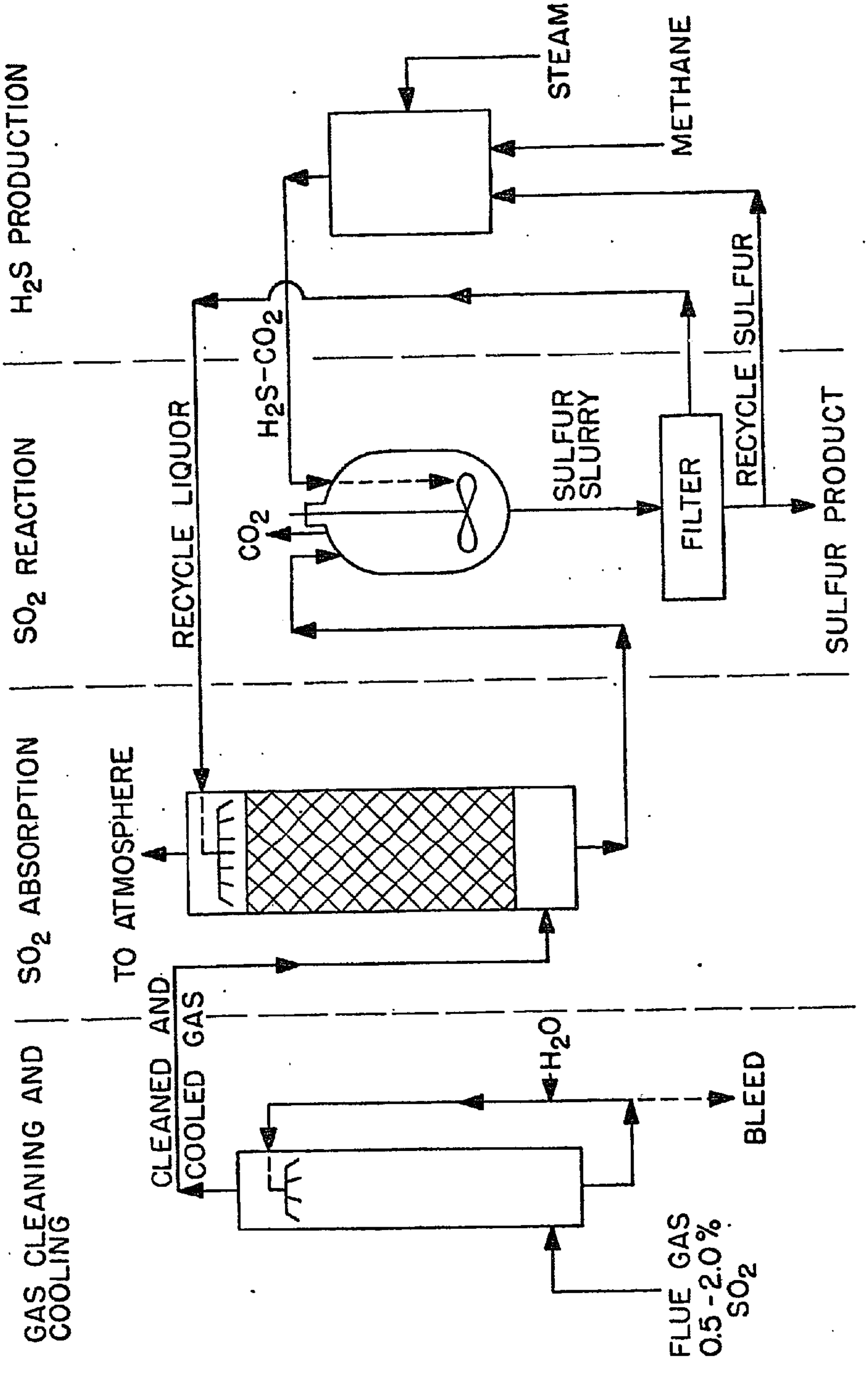
Biochemical fuel cells use bio-organic matter as a source of fuel. Micro-organisms are employed to catalyze the fuel oxidation. Low powers were, however, reported because of a lack of knowledge of biochemical kinetics.

Another attractive projected application involves the use of the abundant sulfur that we are going to collect from the high sulfur coals to fabricate "sulfur fuel cells". Instead of oxidation of hydrogen or hydrazine, one may think of sulfidation of a metal whose sulfide has a large free energy of formation. Catalysis of the sulfidation reaction and of the electron exchange at the sulfide/sulfur phase boundary would enhance the performance of these cells which are otherwise too sluggish to be practicable. Bacteria of the genus "thiobacillus" may be found to accelerate the room temperature electron exchange between sulfides and elemental sulfur. Unless we decide not to be dependent on the moods and irrationalities of a bacteria colony, sulfur fuel cells activated by bacteria may provide economic energy sources. Much needs to be learned, however, about enzyme catalysis and bacteria metallurgy before these goals can be realized.

Catalysis is a congener of chemical kinetics. The Bureau of Mines conducts projects on the kinetics and mechanisms of metallurigical reactions. The objective here again is directed towards lowering the energy requirements of metallurgical processes by determining their activation energies, half-life periods, rate coefficients, etc., and searching for ways and means to lower their activation barriers. The development of promoters and the identification of inhibitors for metallurgical reactions is one way to economize processing time and energy. For blast furnace reactions, small quantities of alkali and alkaline earth oxides were found to accelerate the reduction of iron oxides with CO. We published these findings in the

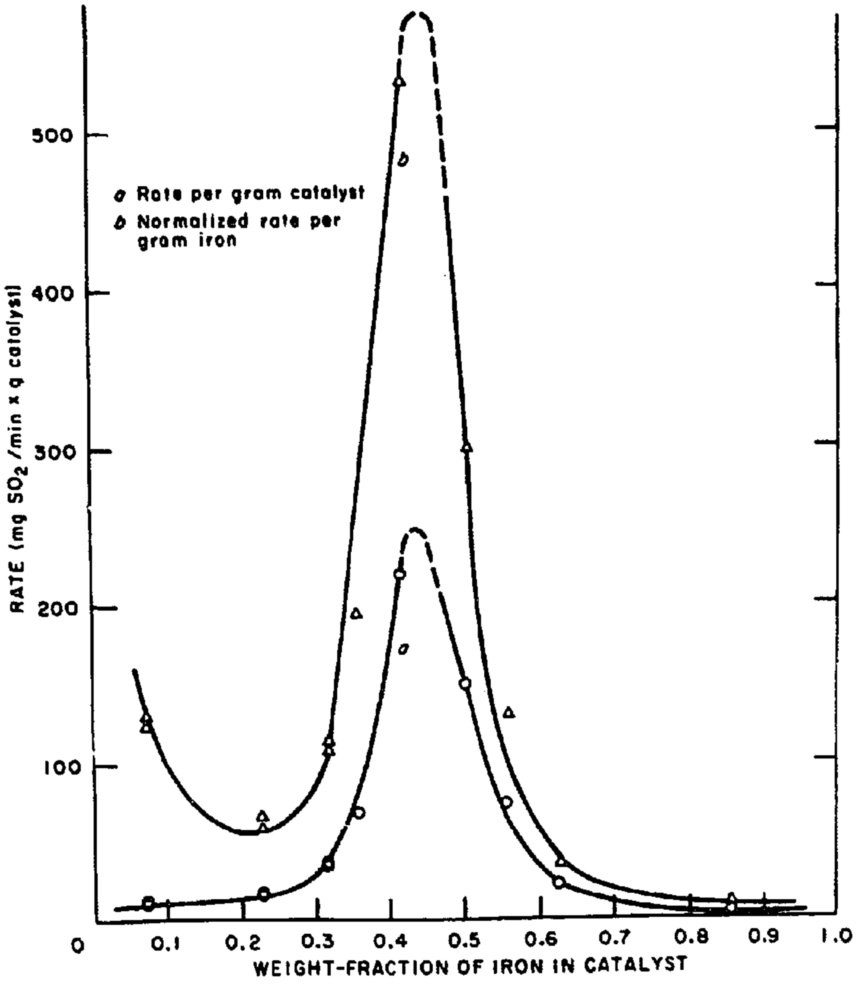
Metallurgical Transactions of 1967. It is interesting to note that these are essentially the same materials previously found by Professor Emmett to promote the iron catalyst for ammonia synthesis. Lately, we also found that small quantities of boron or sulfur retard the basic reduction of iron oxides, and hence they would increase the processing time and energy needed to achieve a given degree of reduction. Removal of the inhibitors and deliverate addition of selected promotors may partially save in the energy demand of a metallurgical process in dynamic operation.

Finally, I hope to have covered, as much as possible, some of the important aspects of catalytic and "near catalytic" research activities at the Federal Bureau of Mines.

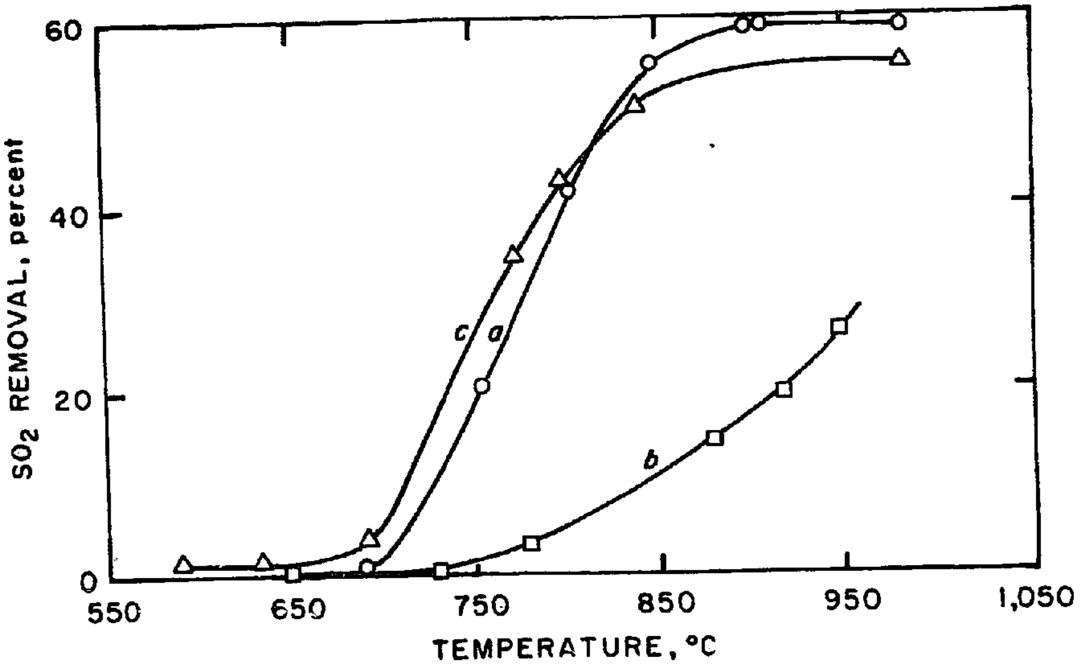


REMOVAL OF SO$_2$ AND PRODUCTION OF SULFUR

1


a Rate per gram catalyst
b Normalized rate per gram iron
a
b
RATE (mg SO_2 /min x g catalyst)
100
200
300
400
500
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
WEIGHT-FRACTION OF IRON IN CATALYST

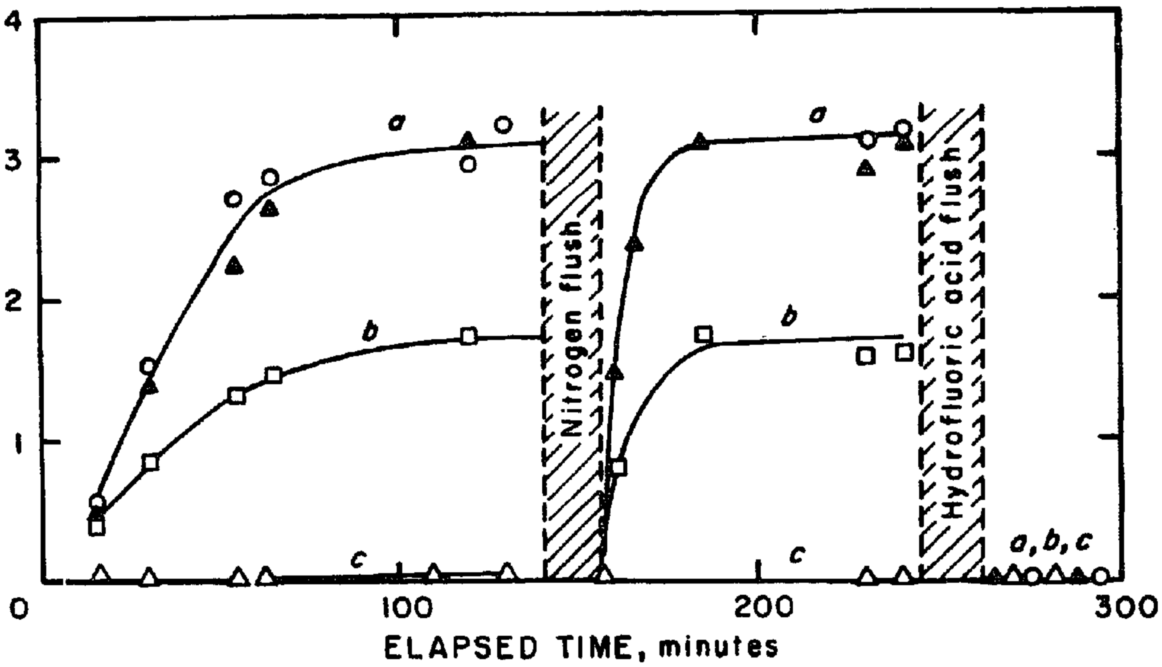
2



Effect of pretreatment on the catalytic activity of Buehler alumina for the SO_2-CO reaction.

a- Untreated (blank); *b*-Treatment in 48% HF; and *c*-Treatment in 99% quinoline

3

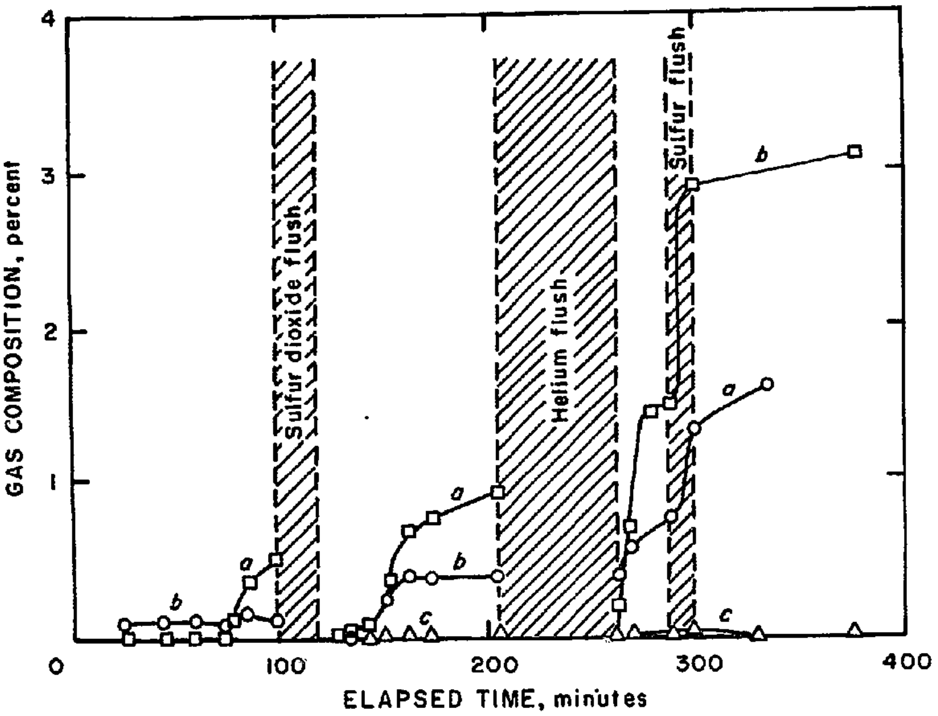


Effect of HF vapor on the catalytic activity of Harshaw alumina at 525°C

a-CO reacted (○); and CO_2 formed (▲);

b- SO_2 reacted; and *c*- SCO formed

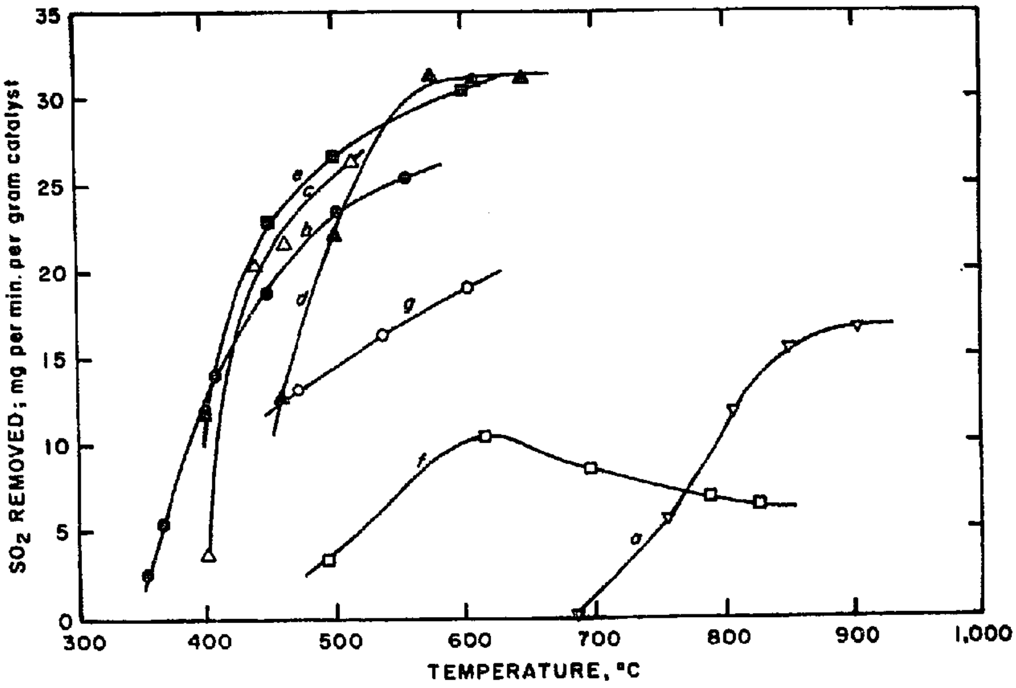
4



Effect of sulfur vapor on the catalytic activity of Harshaw alumina at 540°C

a- CO_2 formed; *b*- SO_2 reacted; and *c*- SCO formed

5



Catalytic efficiency of various alumina containing products for the removal of SO_2

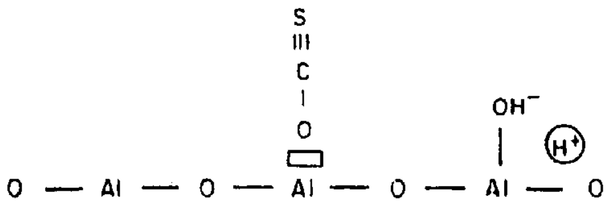
a- Buehler alumina; *b*- 41% iron in alumina; *c*- Jamaican red mud; *d*- Surinam red mud; *e*- Red bauxite; *f*- Zeolite (5A); and *g*- Zeolite (4A)

7

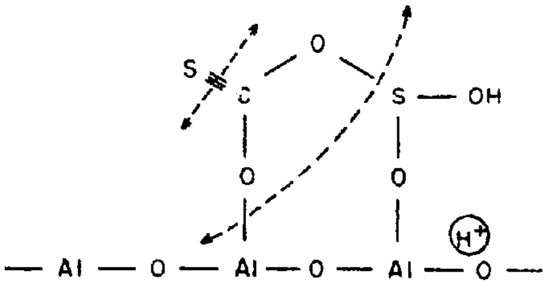
RESONANCE STRUCTURE AND CHEMISORPTION OF SCO

$O=C=S$ I $^{+\delta}O\equiv C-S^{-\delta}$ II $^{-\delta}O-C\equiv S^{+\delta}$ III

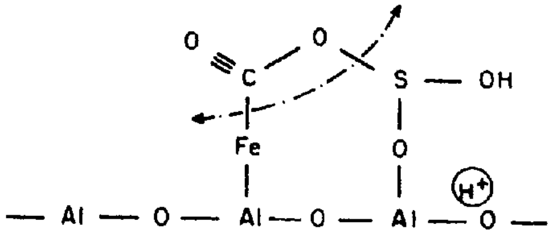
ADSORPTION OF SCO ON ALUMINA LEWIS SITE



REACTION MODEL BETWEEN TWO NEIGHBORING SITES



ROLE OF IRON IN BIFUNCTIONAL CATALYST



THE ROLE OF UNIVERSITIES IN CATALYSIS RESEARCH

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(713) 528-4141

Let me preface my remarks by stating that these are my own ideas about the role of universities in catalysis. It seems that many people have ideas about what universities should do, and you may agree or disagree with some of the remarks I'll make; feel free to discuss them.

The first slide (Fig. 1) deals with academic research in catalysis. Catalysis is certainly not an independent scientific discipline. It involves chemistry, physics, chemical engineering, and materials science; all of these have an imput in catalysis research and must be included in any viable training program. Training in catalysis should include graduate courses in these different departments, and those extra courses may require a longer time to obtain a Ph.D. than it might take in some other field. In addition to these courses, more experimental work is generally involved in catalysis than in other areas. The thesis problem should be a complete story so that a student can feel that it is his own. It should concern publishable material, which brings up the sensitive question of proprietary research. It should require the application of several techniques, and this calls for what several people have described as a "critical mass". It's difficult for one person in a university to have enough of the techniques available to do a decent job in catalysis research, but a person who is properly trained the area should become familiar with more than one technique. The objective of university research is to provide new insights that can lead to an understanding of useful catalytic processes. By useful catalytic processes, I do not mean that the specific project the student works on must in itself be useful, but it should have some practical useful input in the long range. I have borrowed a statement from Professor Boudart, namely "that university or academic research in catalysis is not fundamentally different from long range basic research in industry." The main difference perhaps is that it does not involve process-oriented research. Nevertheless, long range basic research should be essentially the same in both universities and industry. Some of my remarks are taken from a critical article in Chemical Engineering Progress, 1973, by Weiss, Lewis, Meers, and Heck, called, "Industrial Needs in Catalysis", which contains the opinions of a number of industrial people who were asked to appraise academic catalytic research. The article

TABLE I

"The Role of Universities
in Catalysis Research"
Joe W. Hightower

ACADEMIC RESEARCH IN CATALYSIS

1. Catalysis not an independent scientific discipline.

Chemistry	Chemical Engineering
Physics	Materials Science

2. Training should include graduate courses in several departments - may take longer.

3. Thesis problem well-defined.

    Reasonably complete story
    Significant
    Publishable

4. Should involve application of several techniques

    "Critical Mass"

5. Objectives to provide new insights that can lead to an understanding of useful catalytic processes.

6. Not fundamentally different from long-range basic research in industry.

    cf. Weiss, Luss, Mears, Heck
    "Industrial Needs in Catalysis"
    Chem. Eng. Progress 69, 59(1973)

    ...and response by M.Boudart

    cf. AIChE Workshop - J.G. Richardson

Hightower (Continued)

is followed by a response written by Professor Boudart. In addition, this past spring an AIChE Workshop dealing with the same subject was directed by Professor Richardson. The proceedings of this meeting will be published fairly soon; reprints may be obtained from Professor Richardson. Both articles represent critical reviews of university research in catalysis.

Now let's look now at the functions of universities in catalysis (see Fig. 2). The primary function is to supply trained researchers. It's been my observation that most of the industrial catalytic researchers have not been trained in catalysis, but they have become involved in catalysis research after they have worked in industry. This indicates a scarcity of graduates from our universities trained in catalysis. One way to help reduce this shortage is to spur interest by introducing the concepts of catalysis at the undergraduate level. This is not done in most institutions, but it can be achieved by having occasional lectures on catalysis in existing courses, for example, in the chemical engineering kinetics courses, in reactor design courses, and in physical chemistry courses. At Rice last summer we gave an NSF sponsored short course for college teachers which had this as it's objective; feedback has indicated that the course has been at least partially successful in reaching the stated goals.

Another function of universities is to provide updating courses for practitioners of the art, and this will help to open communication channels and serve to train late-comers to the field, e.g. it should be of use to people who have been practicing catalysis for some time but may not be familiar with the most recent techniques. There are a number of short courses in catalysis now being offered at Rice and at several other universities. For example, we are having one in February this next year.

We should also seek a "critical size" in a few outstanding centers, instead of having only a single person doing research in a wide distribution of universities. There should be two or three senior people in a few places. There may be some disagreement on this point, and I'll welcome comments. I've listed a figure of a hundred thousand dollars plus to set up an effective laboratory. Research should involve exploration of fundamental

TABLE II

FUNCTIONS OF UNIVERSITIES IN CATALYSIS

1. Supply trained researchers
   (Most industrial researchers not trained
   in catalysis)

2. Introduce concepts of catalysis at undergrad level.
   - Occasional lectures in existing courses
   - N.S.F. short course for college teachers

3. Offer "updating" courses for practiiners of art
   - Open communication channels
   - Train "late-comers" to field - short courses

4. Seeks "critical size" in a few outstanding centers
   - $100,000 to set up effective laboratory
   - Probably 3 or more

5. Research should -
   - Explore fundamental steps in catalysis
   - Develop new techniques
   - Not become involved in process research

6. Serve as consultants in industrial labs

7. Involve industrial researchers in teaching
   - Seminars
   - AIChE's conferences in catalysis
   - Workshops on university - industrial interaction

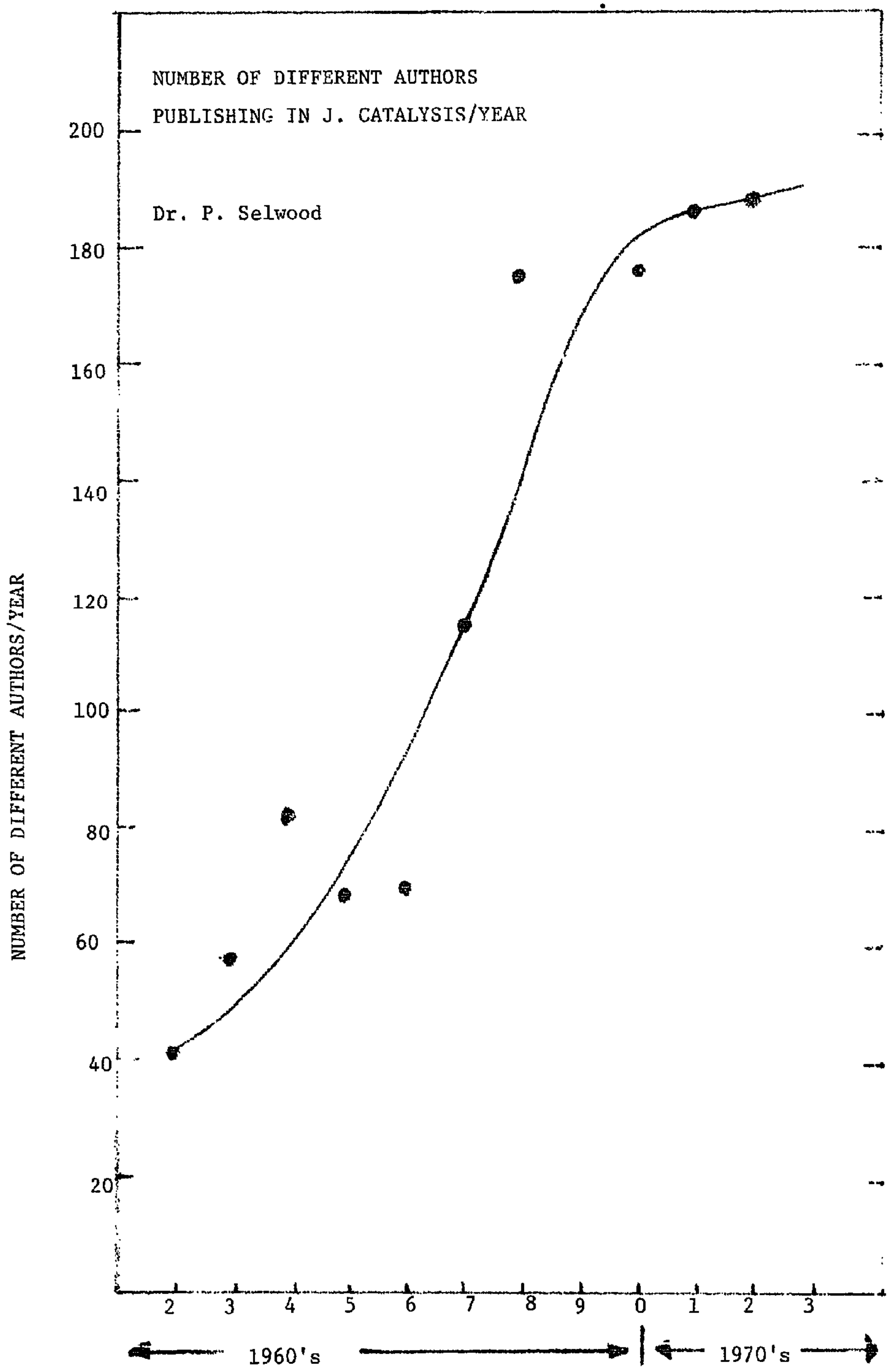
8. Participate in International efforts
   - Exchange of people
   - U.S. - USSR Joint Technology Exchange
   - Latin American assistance

Hightower (Continued)

steps in catalysis and development of new techniques such as those Professor Bourdart has told us about, but it should not be process-oriented. Another thing university people can do is to serve as consultants in industrial laboratories. This will help to open up the communication channels and help to keep the academic people aware of what is important to industry. Another thing we can do is involve industrial researchers in our teaching programs in universities in several ways such as through seminars. An example is the AICHE's Conferences in Catalysis, a program started by Professor Boudart and followed up by Al Weiss and several others in which outstanding industrial researchers visit laboratories for a period of a week for intensive discussions of important problems in catalysis. Another way is through workshops with university-industrial interaction. Again, the AICHE has been involved in this area. Another role that the university people can perform is to participate in international efforts. This could involve the exchange of people, for instance, the U.S.-U.S.S.R. joint technology exchange program and the Latin-American Assistance program in which several have participated. In these ways it is possible to bring expertise that may not currently be available into the United States and make it available to our industrial people, although I think we are as far or further ahead than any other country in industrial catalysis work.

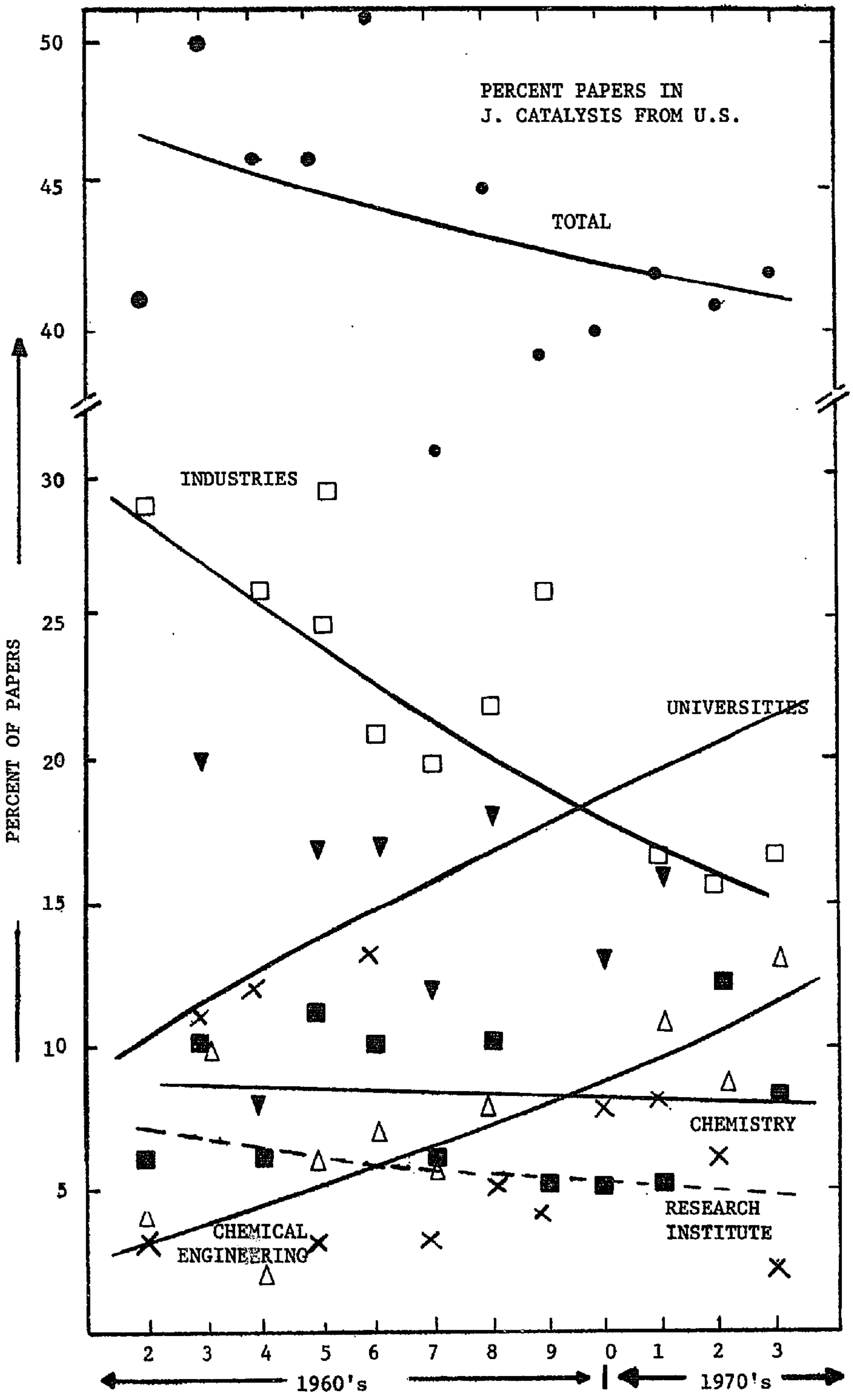
I'd like now to discuss the number of people who are in catalysis and how they are distributed. One source of information is the number of publications in Journal of Catalysis. It may be argued that this is not a fair measure of research effort in catalysis, although I think it's fairly representative. The Editor, Professor Selwood, has given us the number of different authors per year, from 1962 (when the journal began) through 1973 (see Fig. 3). The number of authors has risen and peaked out at somewhat less than 200 people publishing per year, world-wide. These are different authors, not the number of publications, and if there are three or four names on one publication, these count as three or four.

In Figure 4 I've plotted here the percentage of papers and communications in the Journal of Catalysis versus year from 1962 to 1973, that have come from the United States. In '62 it was about 47% but has decreased since then. Figure 5 shows a breakdown by type of organization within the U.S. from which the papers come. Curve A represents the percentage of contributions from U.S. industrial sources; these have decreased from about 30% to near 15%.

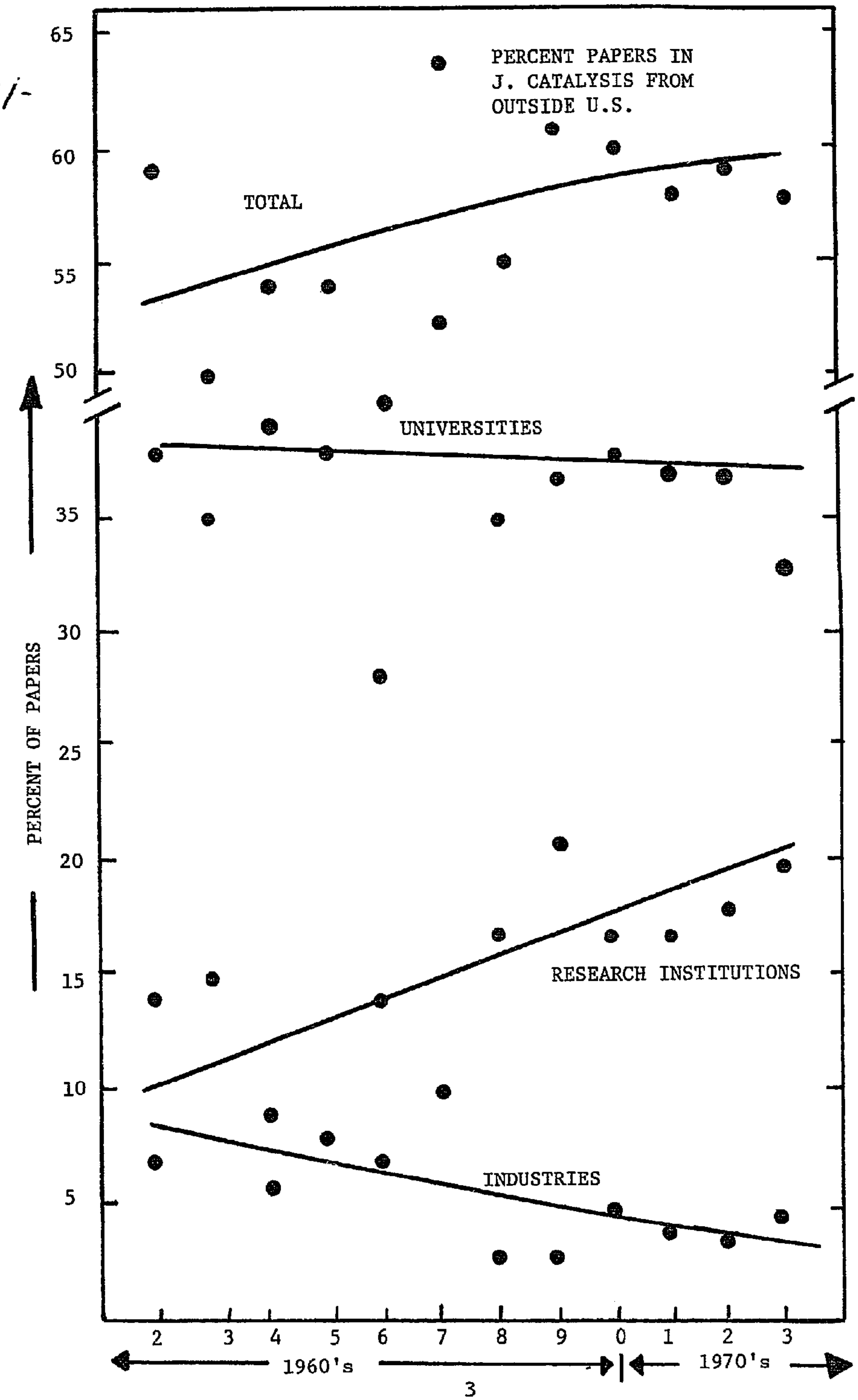

NUMBER OF DIFFERENT AUTHORS
PUBLISHING IN J. CATALYSIS/YEAR
Dr. P. Selwood
NUMBER OF DIFFERENT AUTHORS/YEAR
200
180
160
140
120
100
80
60
40
20
2
3
4
5
6
7
8
9
0
1
2
3
1960's
1970's

1

400



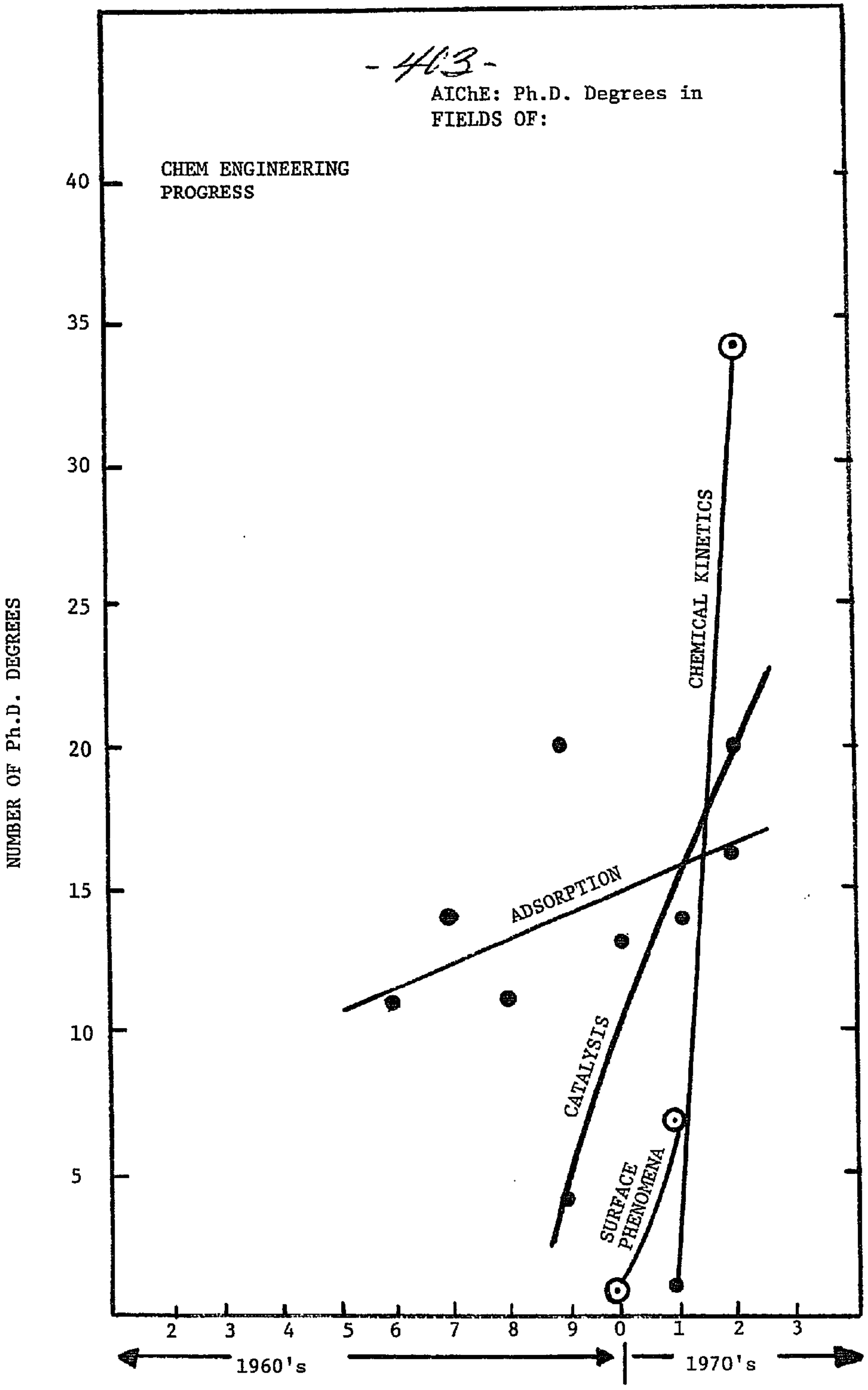
PERCENT PAPERS IN J. CATALYSIS FROM U.S.
TOTAL
INDUSTRIES
UNIVERSITIES
CHEMISTRY
RESEARCH INSTITUTE
CHEMICAL ENGINEERING
PERCENT OF PAPERS
50
45
40
30
25
20
15
10
5
2
3
4
5
6
7
8
9
0
1
2
3
1960's
1970's


PERCENT PAPERS IN J. CATALYSIS FROM OUTSIDE U.S.
65
60
55
50
35
30
25
20
15
10
5
PERCENT OF PAPERS
TOTAL
UNIVERSITIES
RESEARCH INSTITUTIONS
INDUSTRIES
2
3
4
5
6
7
8
9
0
1
2
3
1960's
1970's

SUMMARY: PUBLICATION TRENDS IN

J. CATALYSIS

	U.S.	FOREIGN
TOTAL	↘	↗
INDUSTRIAL	↘	↘
RESEARCH INST.	↘	↗
UNIVERSITIES	↗	→
CHEMISTRY	→	
CHEMICAL ENGINEERING	↗	


AIChE: Ph.D. Degrees in
FIELDS OF:
CHEM ENGINEERING
PROGRESS
NUMBER OF Ph.D. DEGREES
40
35
30
25
20
15
10
5
CHEMICAL KINETICS
ADSORPTION
CATALYSIS
SURFACE PHENOMENA
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1960's
1970's

Hightower (Continued)

Discussions:

Linquist: Another source that would show what industry is doing is the API index of catalysis patents, the numbers granted over the last ten years. I think industry's contributions to publications in the Journal of Catalysis have gone down as industrial success has been achieved, and this is reflected in the number of patents.

Hightower: I wouldn't doubt that at all. This certainly has not shown the entire picture. My plots show only what has happened in the Journal of Catalysis, and I'm reluctant to draw generalizations from them.

Huff: I might suggest another source of information on industrial people. We've mentioned explosives, a research activity that used to be at our center and is no longer. At Pickatinny, for example, there are several people who have done catalytic work on azides and molten salt melts. Now, this is an area of interest to the DOD. I think that you ought to seek out government catalytic researchers and combine them with your other data.

Hightower: Undoubtedly this is correct. Are there any general questions or comments?

Johnson: Just for the record I think the problem should be stated that the Navy uses catalytic oxidation units in all their nuclear submarines and although it is a small use it is extremely important.

Hightower: Yes, are these mainly Hopkalite type catalysts?

Johnson: Well not unless something else changes pretty drastically and I think they are handling the air purification of submarines quite well. They take care of the hydrogen from batteries, carbon monoxide, from smoking and all of the myriad of hydrocarbons and other organic vapors.

Voice: What are you doing about Freon?

Johnson: We're taking care of haloid compounds, the fluoro-carbons, by eliminating certain ones, for example, the tri-chloro and tri-fluoro compounds that are the ethanes often used in industry and in laboratories for cleaning and many other things. These are banned in the submarines. On the other hand, for refrigeration purposes up to the present time we still use these compounds but they are the very resistant ones that will stand the 600 degree temperature in the catalytic burners with very little decomposition. I don't mean to say there are not problems but these problems have been pretty well taken care of so that at the present time we're riding around fairly comfortably and we don't have to replace catalysts ordinarily before the 60 day submergence is up. We use two burners for boats; ordinarily one burner takes care of the carbon monoxide which is the one they really need to control.

Hightower: Thank you very much, Dr. Johnson, for that statement. Is there anything else in a general way that needs to be said? Dr. Huss has told me that they are holding a briefing for industry, called Advanced Planning Briefing for Industry. This will be held in March at Fort Belvoir. Anyone is welcome to attend this meeting, but you have to pay your own way.

Huff: Direct your inquiries to the Commander at the address that is given for me. It will cover everything that we deal with at Fort Belvoir ranging through fuels, lubricants, sanitary sciences, water conditioning, construction equipment and all its problems, a wide variety.

Hightower: Do we have comments from any of the other DOD people? Are there questions that you would like to have discussed, because you probably won't see this collection of catalytic people together again at your disposal for some time. Do we have any questions we would like to address to the DOD?

Libby: Please send your slides. The recommendations of this workshop as compiled by Professor Hightower's panel will be sent you as soon as I am advised by Progessor Joe Hightower that they are ready. Please reformulate them as you wish, critize constructively, suggest omitted research programs and send back as soon as you can and again we will try to have the final recommendations from this workshop out to you as early as possible. We'll send to anyone their comments in the discussion, the pertinent pages. If you do not correct the comments and talks we'll publish it the way it sounded in the taping.

Cohen: Are the recommendations to be limited to the research on catalysis?

Libby: Dr. Cohen, if you have recommendations your feel are important I urge you and everyone else to write them on pieces of paper and give them to Professor Hightower now; his panel will meet the remainder of this afternoon.

Hightower: Let me add this; suppose we are given a large number of recommendations. Let's take the highly unlikely case that we don't feel that some of them are very relevant, then the panel should reserve the right to include which ever of these it sees fit. The panel will have the final say on this but we welcome and encourage you to make inputs anyway you feel appropriate.

Quillian: I would recommend that you categorize recommendations regarding the basic exploratory research. It will give better organization and make it much simpler for the military people to recognize the significance.

Hightower: Shall we scratch everything that was basic everything except for what was applied?

Quillian: What are the instructions, probably basic versus exploratory.

Voice: Well basic research is research in mechanisms without any prospect or application at all. Exploratory depends on length of that application. Applied research ... I have no business describing that, someone from the DOD should be doing this.

Burwell: It seems to me this basic problem exists and has not been fixed. Now I suppose everybody can agree that almost all of the chemical reactions which procede uncatalized have been discovered. The new ones are almost all going to be catalytic and the new industrial processes will surely be almost all catalytic as indeed they have already been for the last fifteen years. But now why should DOD worry? They might on the one hand perfectl well think that everything is going along well and Dr. Haensel's groupd turns out all the needed developments and products and the DOD is going to buy the products so they don't need to worry about it and that could be a perfectly reasonable conclusion from their point of view. It would only be if things are not going reasonably well that I would assume that DOD needs to address itself to the problem at all. And this is exactly what we've not covered; now I may be cuckoo but that's my reaction.

Lauriente: You have to quantify your results with time scale. Then this becomes competitive with the other programs that are put in the hopper when the day comes for bidding for funds.

Holliday: Doesn't that pretty much rule out basic research if that's the criteria you want to apply?

Haensel: In connection with the recommendations you and your group are going to make I think there should also be some that will be geared to a minimum program as well as a maximum program. In other words the highest priority should be such and such area corresponding to the funds that may or may not be available, may be a sort of guide line for your deliberations.

Burwell: It might be interesting or amusing for you to compare after we've seen these proposals, a similar exercise sponsored by NATO last year. There was a meeting held less than a year ago in Sardinia which covered the hetrogeneous and also homogeneous and metallo-enzimes. Agains, various recommendations were made about what should be done and this is published in a volume of Plenary Press but there was no publicity as far as I know. Professor Boudart says the report is not quite as bad as he expected.

Hightower: Are there any other comments. I'd like to certainly thank Leona Libby, R&D Associates, Billie LoPinto and all the people here who have been involved, and above all, all you speakers and commentators for hanging with us. We appreciate it very much. Thank you.

Libby: Thank you all. RDA is honored and grateful. Thank you very much.

APPENDIX A

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CATALYSIS

4/10

Substances that accelerate chemical reactions without being used up play a major role in producing goods worth more than $100 billion a year. Various techniques help to reveal how a catalyst functions

by Vladimir Haensel and Robert L. Burwell, Jr.

When a chemist considers a chemical reaction, he generally asks himself three questions: How fast is it? How complete is it? How selective is it? Some reactions are very fast and go to completion to yield a single product. A familiar example is the reaction of sodium and chlorine to form sodium chloride. Other reactions, for instance the reaction of hydrogen and oxygen to form water, go very slowly at room temperature but are extremely fast at higher temperatures. They eventually go to completion to yield a single product. Most reactions are very slow indeed. The chemist has to find ways to speed them up. If he is lucky, he can do that simply by raising the temperature (as in the reaction of hydrogen with oxygen). Unfortunately increasing the temperature frequently produces undesirable side effects.

Two major reasons for seeking alternative means of speeding up chemical reactions can be illustrated by the following examples. One is the reaction of nitrogen and hydrogen to form ammonia (NH_3). The other is a hypothetical reaction between methane (CH_4) and oxygen to form dimethyl ether (CH_3OCH_3) and water. Both reactions are alike in that at room temperature their rate is essentially zero. The laws of thermodynamics tell us, however, that both reactions should go a long way toward completion at room temperature.

Let us see what happens as we raise the temperature with each of these reactions. In the reaction forming ammonia there is a composition (some specific proportion of H_2, N_2 and NH_3) that is in chemical equilibrium at a given temperature and pressure. Other compositions, if they react, must tend toward the equilibrium composition. Suppose one raises the temperature in an attempt to get a reasonably good yield of ammonia in a reasonable period of time. Before the rate of formation of ammonia becomes fast, the position of equilibrium has shifted to increase the proportion of hydrogen and nitrogen at the expense of ammonia [*see top illustration on page 48*]. For practical purposes, then, one cannot cause nitrogen and hydrogen to combine directly to form ammonia.

In the second reaction other oxidation reactions of methane become fast as the temperature is raised and destroy the methane before detectable amounts of dimethyl ether are formed. In general most possible reactions proceed slowly at room temperature, and the great majority of reactions in this class cannot be practically effected by raising the temperature. For such reactions what one lacks is selectivity.

If nature provided no way to accelerate chemical reactions selectively, our modern technological society could not have arisen, but one must quickly add that its absence would not be noticed because no form of life could exist either. In fact, nature long ago discovered how to effect many reactions of the type that cannot be effected merely by raising the temperature. Man has acquired the knack only recently.

If the mixture of hydrogen and oxygen is exposed to platinum powder at room temperature, a rapid reaction forming water occurs on the surface of the metal particles. A few atoms of platinum can lead to the formation of many molecules of water. This is catalysis, defined as the phenomenon in which a relatively small amount of foreign material, called a catalyst, augments the rate of a chemical reaction without itself being consumed. The chemist now has an alternate means at his disposal for speeding up reactions. How do these catalysts work?

Suppose one knows that two chemical substances, A and B, react to form C but that the reaction is extremely slow at room temperature. One can demonstrate that no combination of elementary processes involving A, B and C will result in rapid formation of C. Now add a catalyst, designated Cat. It provides the possibility of new elementary processes. If processes such as the following are fast, C will be formed rapidly:

$$A + Cat \rightarrow ACat$$
$$ACat + B \rightarrow C + Cat$$

The combining tendency of A and Cat must be adequate to yield the complex $ACat$, yet it must be not so strong as to make $ACat$ unreactive. After all, unless $ACat$ reacts rapidly with B to form C and then regenerate Cat, we do not have catalysis.

Chemists must by now have discovered the great majority of reactions that proceed without catalysts. Clearly the future of preparative chemistry will heavily involve catalysis. We already have a catalyst (iron) that enables us to manufacture ammonia, but we know of no catalyst that leads to the formation of dimethyl ether from methane and oxygen. There are almost innumerable other reactions that have favorable positions of equilibrium but for which no catalysts are known.

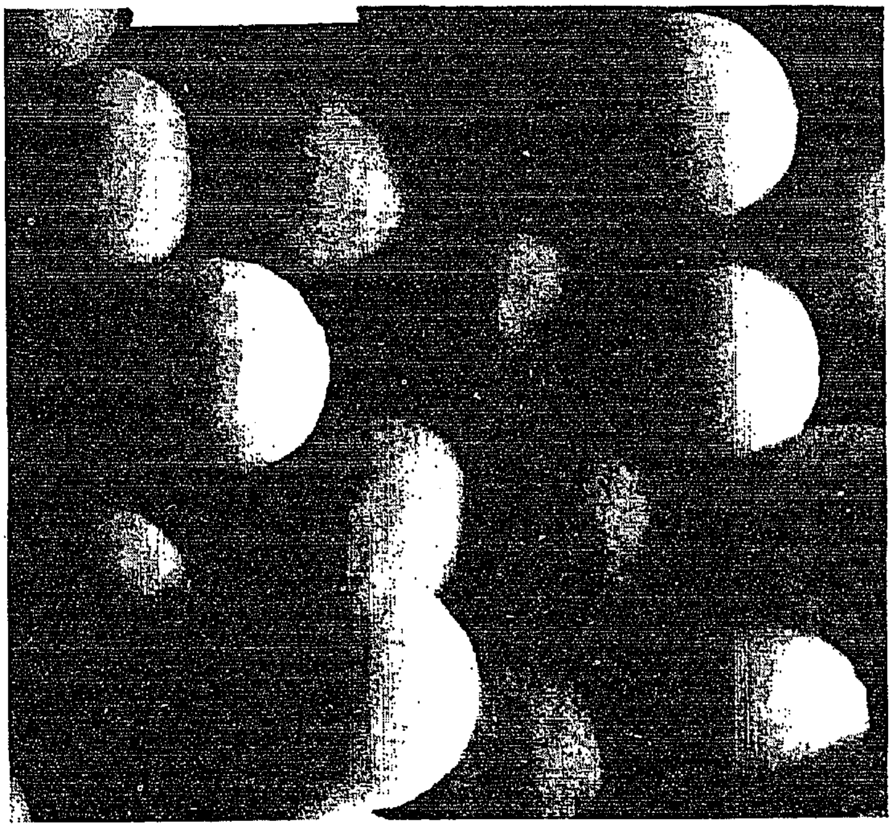
Catalytic reactions can be classified into three principal types. The most common is heterogeneous catalysis, in which the catalyst is a solid and the reactants and products are either gases liquids. Platinum is a heterogeneous catalyst for the reaction between hydrogen and oxygen. The second type is homogeneous catalysis, in which the reactants, products and catalyst are molecularly dispersed in a single phase, usually the liquid phase. The third type is enzyme catalysis, which is found in living systems. There the catalyst is a complex protein molecule (an enzyme) consisting of scores or hundreds of atoms. Connections between enzyme catalysis and other types are beginning to appear, but at the moment enzyme catalysis forms a separate subject. We shall not take it up here.

The Economic Value of Catalysis

Catalysis has grown at a phenomenal rate because it has made possible the production of new chemicals and the mass production of established chemicals. Today it is an indispensable industrial tool. Catalysis contributes directly and indirectly to products accounting for a sixth of the value of all goods manufactured in the U.S.; therefore it participates in economic activities involving the exchange of more than $100 billion per year. The average consumer has little realization that the synthetics he uses every day have been made possible largely through the use of catalysis. They include plastics and fibers, detergents, hydrogenated fats and synthetic rubber.

The petroleum industry provides an outstanding example of the importance of catalysis. Crude oil contains millions of different hydrocarbon molecules of all shapes and sizes. Those with only one to four carbon atoms in the molecule (for instance methane, ethane, propane and butane) are gases at room temperature. Those with five to ten carbon atoms in the molecule boil in the gasoline range (between 20 and 200 degrees Celsius). This fraction of the crude oil ("virgin naphtha") amounts to less than 20 percent of the total; if it were simply separated by fractionation, it would make a very inferior gasoline. Its properties can be improved by subjecting it to a catalytic process called reforming, which we shall describe below. The bulk of the crude oil (about 80 percent) boils in the range between 200 and 600 degrees C. A part of this material serves as heating fuel; another part, after suitable refining, serves as jet fuel and diesel fuel; a small fraction serves as lubricating oil. By far the major part of the oil boiling in the 200-to-600-degree range is converted into gasoline by one or another type of cracking process.

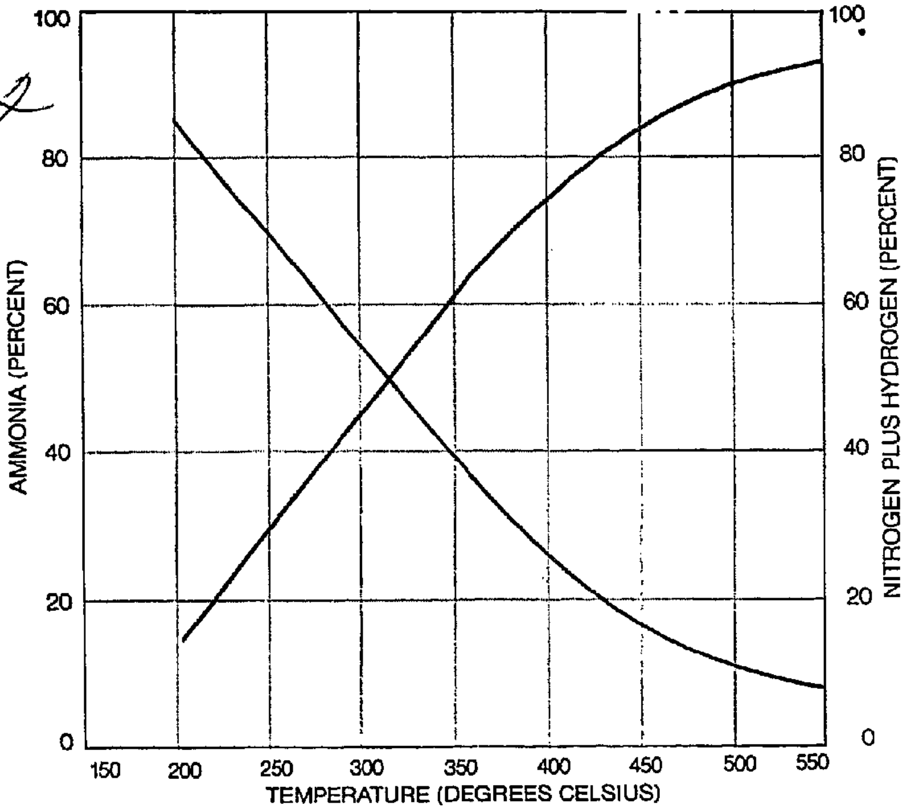
Cracking can be achieved simply by heating the oil to a temperature of about 500 degrees C. under pressure. A much better gasoline and a higher yield can be obtained by doing the cracking in the presence of a catalyst. Thermal cracking, which involves heating the oil to the decomposition point, can be considered



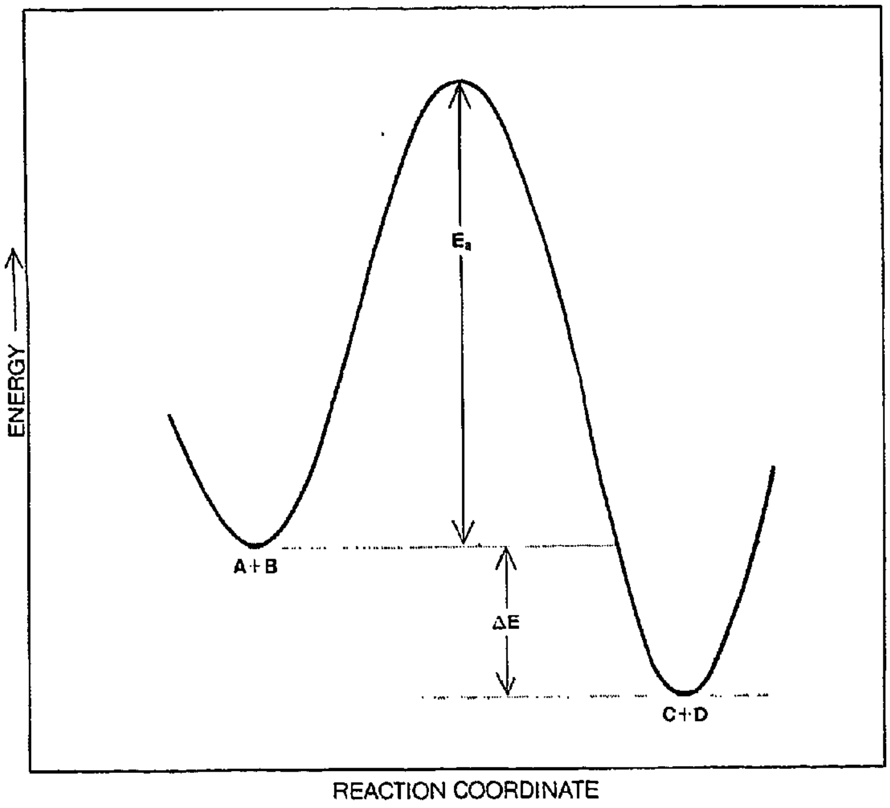
REFORMING CATALYST converts "virgin naphtha," a naturally occurring fraction of crude oil with a low octane number, into high-octane motor fuel. Known as a dual-function catalyst, it alters the structure of hydrocarbon molecules from less favorable (low octane) to more favorable (high octane) configurations. The sample shown here, magnified about 20 diameters, contains .5 percent platinum and 1 percent chlorine on spheres of alumina.

SURFACE OF DUAL-FUNCTION CATALYST is shown at a magnification of 55,000 diameters in this scanning electron micrograph. One can see the enormous surface area that such a catalyst presents. The catalyst is made by the Universal Oil Products Company.

412



EFFECT OF INCREASING TEMPERATURE on an equilibrium mixture of nitrogen (N_2) and hydrogen (H_2) is to shift the equilibrium to yield increasingly less ammonia (NH_3). Without a catalyst ammonia is formed too slowly even at 550 degrees Celsius to provide a useful process. The equilibrium is shown here for a pressure of 100 atmospheres.



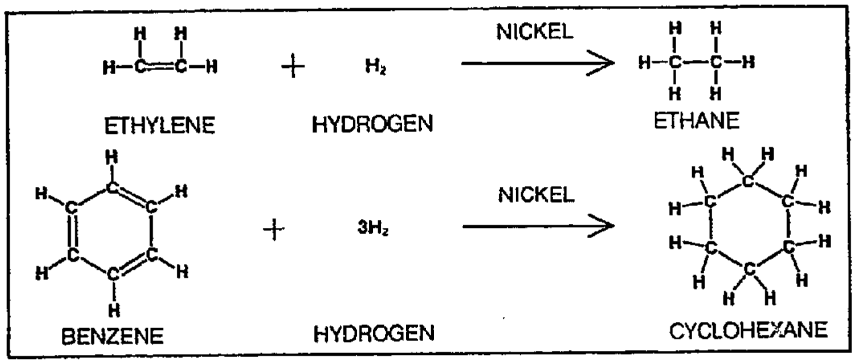
IDEALIZED CHEMICAL REACTION, $A + B = C + D$, requires an activation energy E_a. The potential energy of $A + B$ is at the bottom of the valley at the left, that of $C + D$ is in the valley at the right. A and B can surmount the energy barrier only if they collide with a kinetic energy at least equal to E_a. The barrier is many times greater than the average energy of collision. A catalyst can provide new elementary processes with lower values of E_a.

a sledgehammer approach. Heating in the presence of a catalyst is more sophisticated. Heavy molecules are broken in places dictated by the nature of the catalyst; hence there is a more selective cracking and more pieces boil in the gasoline range. Furthermore, many of the pieces no longer resemble the parts of the original molecule in shape. During catalytic cracking they undergo an isomerization reaction (a molecular rearrangement without change in molecular weight). This change in molecular structure fortunately leads to a better gasoline. If the energy in the fuel is released too quickly, the piston in an automobile engine cannot respond and the energy is expended against the walls of the cylinder, causing a pinging sound ("knock"). Isomerization increases the compactness of gasoline molecules, thereby improving the fuel's antiknock quality [*see illustration on page 50*].

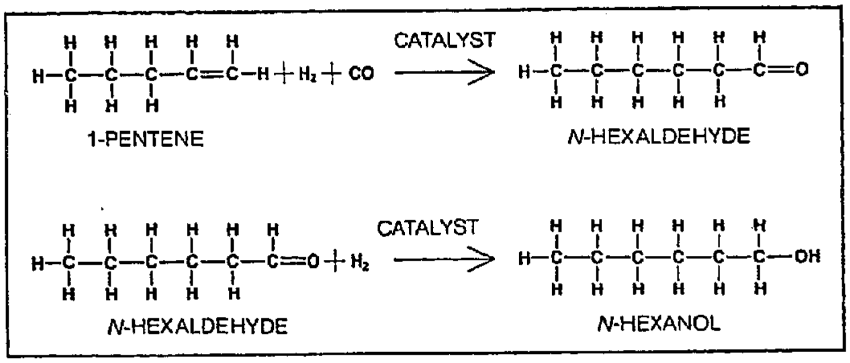
Catalytic cracking is thus a more selective tool in the fragmentation reaction and the fragments are reassembled into more valuable pieces. Since very few reactions are perfect, a catalyzed reaction is no exception and some pieces are too small to be included in the gasoline. Some of these pieces do not have a full complement of hydrogen, so that two of the adjacent carbon atoms are double-bonded. It has been found that the unsaturated molecule (known as an olefin if it has a single double bond and an open structure) can react with another unsaturated molecule to produce a dimer or a trimer in the presence of a catalyst such as phosphoric acid, so that the resulting larger molecules boil in the gasoline range. It has also been found that the unsaturated molecules can be catalytically condensed with the more compact type of saturated hydrocarbons in the presence of sulfuric acid or hydrofluoric acid, but not with the straight-chain saturated hydrocarbons. On the other hand, the straight-chain saturated hydrocarbons can be catalytically isomerized to more compact structures and then reacted with the unsaturated molecules [*see top illustration on page 51*]. Thus a good share of the smaller pieces are reconverted into larger molecules and used as gasoline components. In this manner the original large molecules, by a sequence of number of catalytic steps, are converted into the desired product.

The above discussion has identified only a part of the catalytic participation in the refining of petroleum, but it is clear that if one could tag a few carbon atoms in the original crude oil, they would be seen to go through a complex series of catalytic steps before winding p in a motorist's gas tank. In the U.S. alone some 12 million barrels of crude il are processed daily, virtually all of it eing consumed as an energy source. A small part of this amount, particularly the largest molecular sizes, is used as asphalt and petroleum coke. The smaller fragments from the various cracking steps are gathered, and some, as indicated above, serve to make gasoline. The smallest reactive fragment, ethylene, is used for the production of ethyl alcohol and polyethylene. Much of the polyethylene is made catalytically; it consists of from about 1,500 to 15,000 ethylene molecules strung together in a long chain.

A challenging and timely problem is how to apply catalysis in air-pollution control. At the moment it appears that catalysis will be heavily involved in the treatment of exhaust gas from internal-combustion engines. This will represent the first instance of the direct application by the general public of prepared catalysts, as distinguished from natural catalysts such as yeast.



CATALYTIC HYDROGENATION was discovered by Paul Sabatier in the 1890's. He found that in the presence of nickel, ethylene, the simplest olefin, reacts rapidly with hydrogen to form ethane (*top*). Benzene reacts with hydrogen to form the saturated ring compound cyclohexane (*bottom*). Many industrial hydrogenation processes use nickel as a catalyst.



OXO PROCESS, developed in Germany in the 1930's, involves the addition of carbon monoxide and hydrogen to olefins (here 1-pentene) to produce long-chain alcohols. The reaction is now used to produce intermediates for synthetic lubricating oils and plasticizers.

Early Developments

Having established the substantial contributions of catalysis to the economy, let us briefly trace the history of catalysis. After some 20 years of observing a number of "notable discoveries," Jöns Jakob Berzelius named and defined catalysis in 1836. The contemporary investigator of catalysis is frequently awed by the keen insights of early workers. After defining catalysis Berzelius proposed, among other suggestions, that it involves the development of a force of affinity coming from the catalyst and having an effect on the chemical activity of the reagents.

The "notable discoveries" described by Berzelius included the work of Johann Wolfgang Döbereiner, who in 1823 found that a stream of hydrogen mixed with air would ignite on contact with platinum sponge. In fact, this discovery led to a lamp in which hydrogen was produced from zinc and sulfuric acid, then catalytically ignited to serve as a replacement for the tinderbox for ighting lamps and candles. It is too bad hat such an ingenious device had to be replaced with the match. Other evilence of the catalytic properties of platinum were discovered independently by Humphry Davy and Michael Faraday. All these workers recognized that there was something special, an action through touch or contact, that caused a reaction to occur.

Catalysis received little academic attention during the 60 years following the definition by Berzelius. There were, however, a few technological developments. The heterogeneous catalytic oxidation by air of hydrogen chloride to chlorine ($4HCl + O_2 = 2H_2O + 2Cl_2$) was developed by Henry Deacon in 1868. The direct oxidation of sulfur dioxide with air using a platinum catalyst was observed by Teregrine Phillips in 1831 and restudied by Clemens Winkler in 1875. There was no successful commercial installation of a direct oxidation process, however, until 1901.

As the 19th century ended, the rising importance of the chemical industry stimulated a few chemists to devote their full time to catalysis. Two of the most prominent were Paul Sabatier and Vladimir N. Ipatieff. It is perhaps fair to say that they did more than anyone else to bring catalytic science and technology together.

Sabatier's investigations of catalysis stem from the work of Ludwig Mond, a German-born British chemist, who in 1890 prepared volatile nickel carbonyl: $Ni(CO)_4$. Lord Kelvin remarked that "Mond and his colleagues have given wings to a heavy metal." Sabatier thought it should be possible to synthesize an analogous compound of nickel and ethylene: $Ni(C_2H_4)_4$. Instead of obtaining the desired compound Sabatier found that in the presence of nickel some of the ethylene (C_2H_4) was converted into its fully hydrogenated analogue, ethane (C_2H_6).

Sabatier quickly recognized that if he deliberately introduced hydrogen into the reaction, his nickel catalyst should convert ethylene into ethane with a high yield. Before long Sabatier demonstrated that nickel acted as a general catalyst for the hydrogenation of a variety of unsaturated (hydrogen-deficient) hydrocarbons [*see upper illustration above*].

Ipatieff, who was only 13 years younger than Sabatier, worked in Russia from 1890 to 1929 and in the U.S. from 1930 to 1952. Ipatieff reported the catalytic dehydrogenation of alcohol in 1901. Subsequently he devised industrial processes for the high-pressure hydrogenation of a wide variety of organic compounds. To design the high-pressure autoclaves required by his process, Ipatieff drew on a knowledge of gun barrels he had acquired as a young officer in the

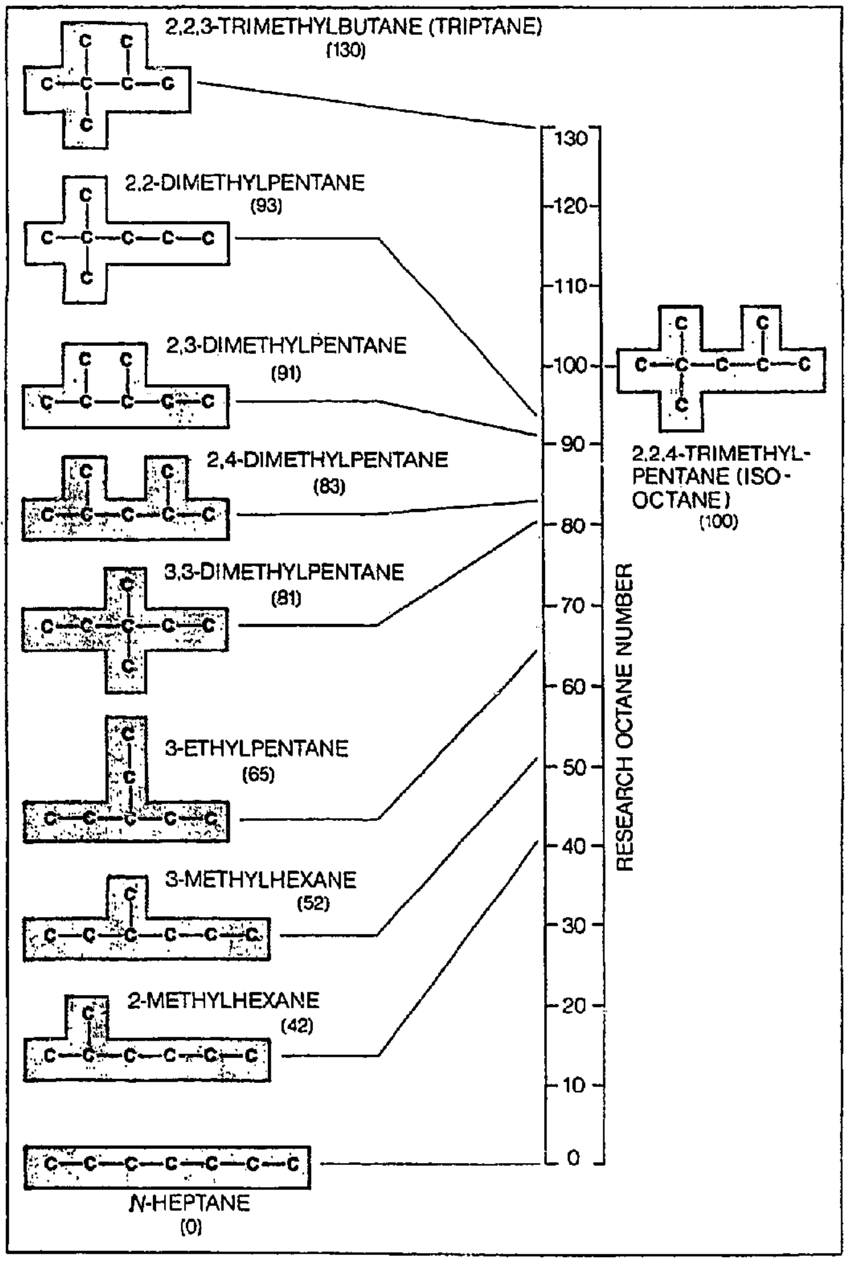
Russian artillery. Building on the foundations laid by Sabatier and Ipatieff, Friedrich Bergius developed the coal hydrogenation process, which supplied Germany with an important part of its motor fuel during World War II.

A goal of many chemists around 1900 was the synthesis of ammonia from hydrogen and nitrogen. The man who first succeeded was Fritz Haber. He worked out a process in the years between 1905 and 1908, testing thousands of potential catalysts at various temperatures and pressures. The first industrial unit incorporating his process was built in 1913. The conversion of ammonia into nitric acid was already commercial in 1906, so that by the start of World War I, Germany was no longer dependent on Chilean saltpeter as a source of nitrates for explosives. Haber's motivation—to make Germany independent of foreign supplies of a crucial industrial material—was a far cry from the innate curiosity that motivated the first workers in the field of catalysis barely 80 years earlier.

The year 1915 marks the entry of physical chemists into the field of catalysis, which had previously been dominated by inorganic and organic chemists. The elegant and precise measurements made by Irving Langmuir of the adsorption strength of various simple molecules on metals gave rise to concepts of chemisorption, and this was further developed by H. S. Taylor, Eric Rideal, P. H. Emmett and a number of other brilliant workers. Their investigations provided further impetus to technological progress.

The 1930's saw a marked spurt in the technological applications of catalysis both in Europe and in the U.S. Significant advances were made by Ipatieff and his co-workers in the use of catalysis for the production of high-octane gasoline. In Europe one of the most interesting new catalytic processes was the Oxo reaction, which involves the addition of carbon monoxide and hydrogen to olefins to produce primary alcohols [*see lower illustration on preceding page*]. The Oxo catalytic reaction is homogeneous, since a soluble cobalt-carbon monoxide catalyst $[Co_2(CO)_8]$ is employed. It was also the first industrial catalytic process to use complexes of transition metals rather than the metal itself. The transition metals (such as vanadium, cobalt, titanium, manganese chromium and copper) are unusual in that they can either lend or borrow electrons with equal ease. The Oxo reaction is now used on a substantial scale to produce intermediates for synthetic lubricating oils and plasticizers.

One striking example of the ability of catalysts to perform highly selective molecular alterations is the stereoregular polymerization of olefins pioneered by Karl Ziegler and Giulio Natta, who were awarded the Nobel prize in chemistry in 1963 for their work. Propylene can be converted to three distinct head-to-tail polymers that differ only in the relative placement of their appended methyl groups. By using suitable complexes involving ions of transition metals, one can produce either "isotactic" or "syndiotactic" polypropylene [*see top illustration on page 54*]. If the starting material is 1,3-butadiene, four different stereotactic polymers can be generated, each requiring a different transition-metal catalyst [*see bottom illustration on pages 54 and 55*]. It is likely that the future will provide many additional examples of the unique capabilities of such catalysts.



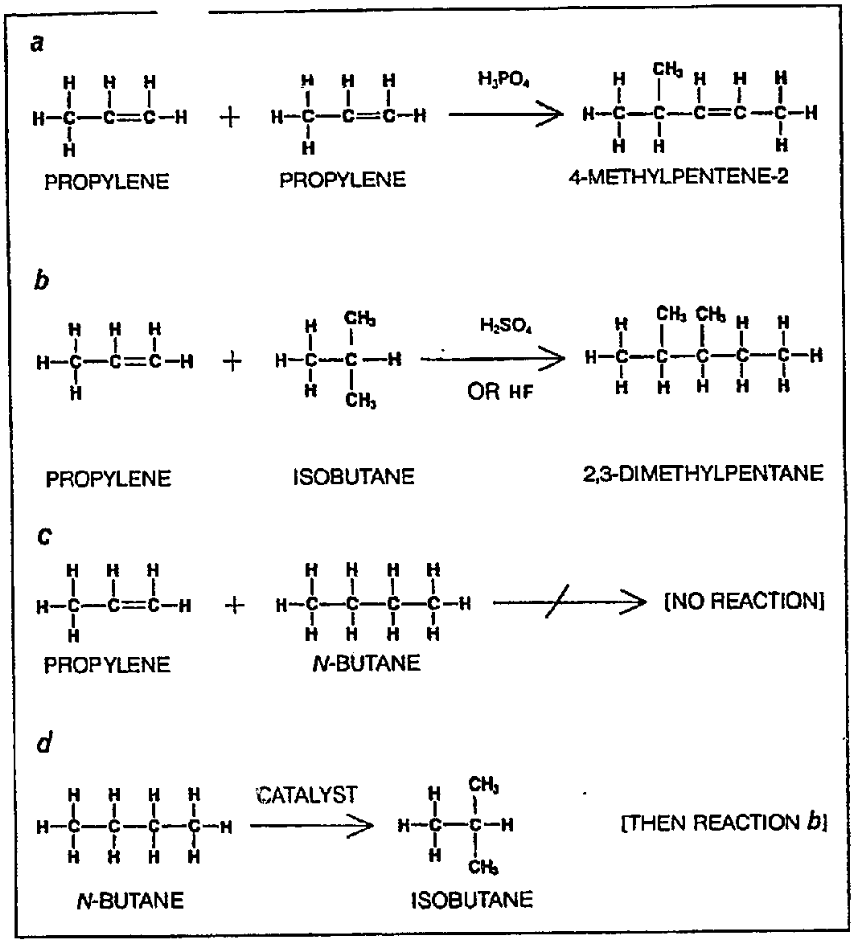
OCTANE-RATING SCALE assigns to normal heptane a value of zero and to iso-octane a value of 100. Hydrocarbons with side chains burn more slowly than straight-chain hydrocarbons and thus tend to "knock" less in automobile engines. The nine possible isomers (structural variants) of heptane are shown; hydrogen atoms are omitted for clarity.

The Mechanism of Catalysis

What makes catalytic reactions go? Like chemical reactions in general, catalytic reactions proceed by a more or less complicated combination of elementary steps. Each step is elementary in that it takes place without intervening intermediates of significant lifetime. Few chemical reactions involve just a single elementary process. Catalytic reactions, then, proceed by means of a set of one or more intermediates. A simple hypothetical example of this was given at the beginning of the article: the reaction $A + B = C$ by way of the intermediate *ACat*. If a foreign substance is to act as a catalyst, it must provide new elementary processes leading to an overall reaction that is faster than the reaction that would take place if only the pure reactants were present.

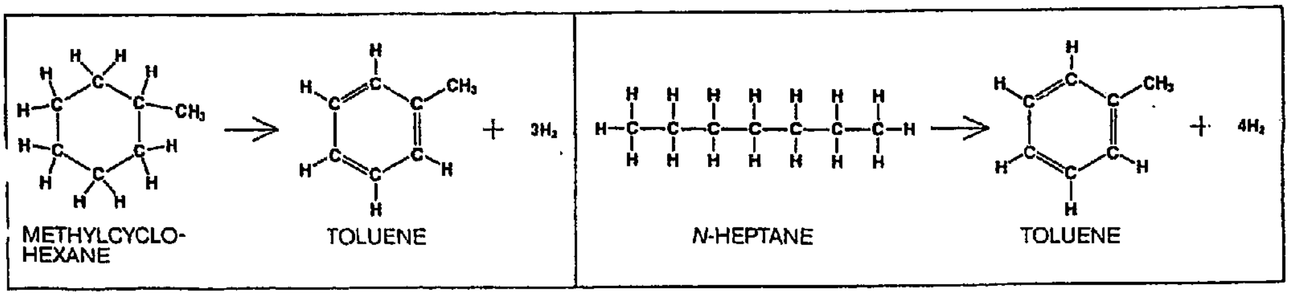
A detailed description of a chemical reaction is referred to as its mechanism. The chemist's views concerning the precise nature of the elementary processes that comprise a mechanism are constantly changing as new facts emerge from studies of catalytic systems. It is usual to recognize five stages in a heterogeneous catalytic reaction: (1) diffusion of reactants to the surface of the catalyst, (2) chemisorption of reactants, (3) surface reactions among chemisorbed species, (4) desorption of products, (5) diffusion of products from the surface.

The diffusion steps can limit the overall rate. In laboratory work one usually tries to make steps 1 and 5 faster than the other steps, but it is often impracticable to translate the laboratory techniques into engineering practice in industrial reactors.

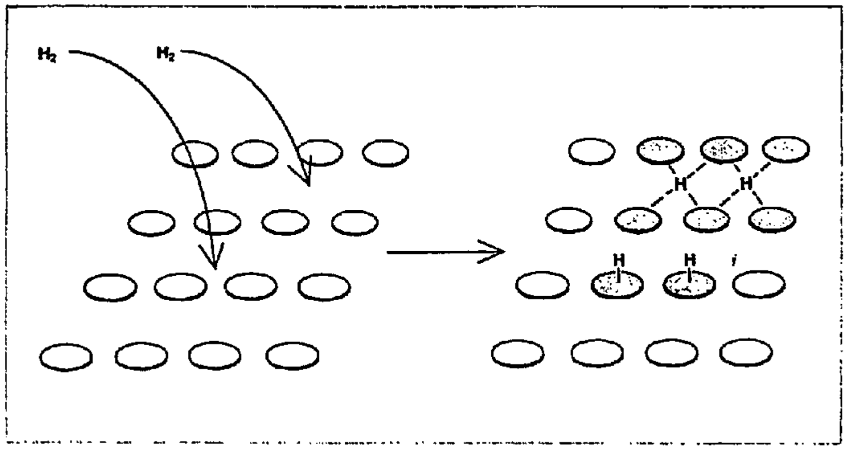


ONE ROUTE TO HIGH-OCTANE FUEL is to assemble small, volatile molecules into larger ones that boil in the gasoline range. Using phosphoric acid as a catalyst (*a*), light olefins such as propylene can be condensed into branched-chain olefins useful as a motor fuel. Either sulfuric acid, $H_2(SO)_4$, or hydrofluoric acid, HF, will join a light olefin to a saturated branched-chain compound (*b*), yielding a product with a high octane number. If the saturated molecule has a straight chain (*c*), no reaction takes place. By isomerization, however, the straight-chain molecule can be rearranged into a molecule that will react (*d*).

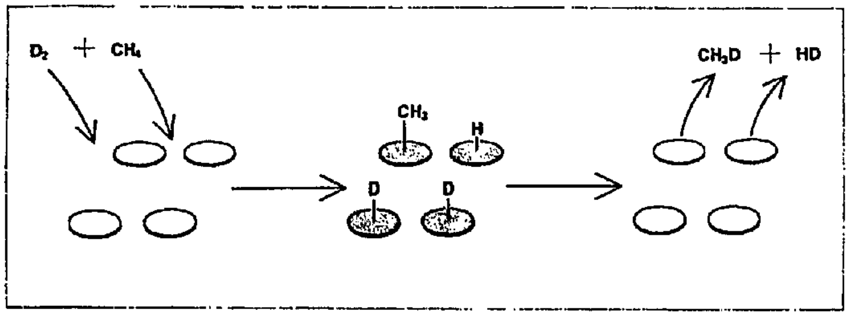
The division of adsorption into physisorption and chemisorption follows the usual division of phenomena into physical and chemical. A physisorbed species retains substantially its original structure. Thus its infrared spectrum will be reasonably related to that of the unadsorbed molecule. The heat of adsorption is small, but not much greater than the heat of liquefaction. A chemisorbed species is a surface chemical compound. The heat of adsorption can be very small or very large, as with the heat of chemical reactions in general. There may be substantial changes in structure between desorbed and adsorbed species; frequently the adsorbed species is only a fragment of the original molecule. Molecular hydrogen (H_2), for example, often adsorbs to form a surface hydride [*see top illustration on next page*]. Chemisorption of this type is called dissociative adsorption. At least one of the reactants must be chemisorbed, but it is difficult to decide when chemisorption is an elementary process and when it



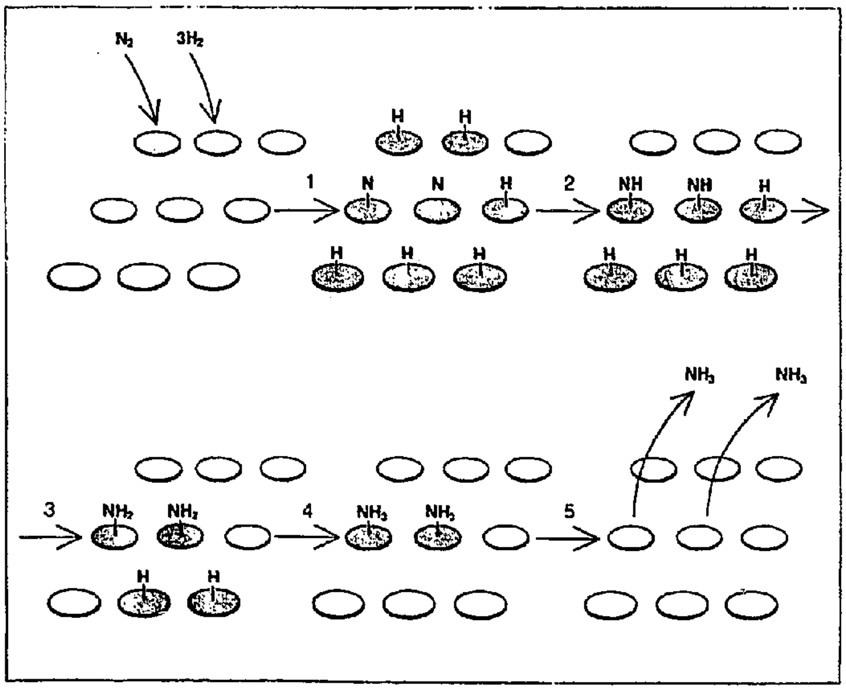
OTHER ROUTES TO HIGH-OCTANE FUEL make use of reforming catalysts that dehydrogenate saturated ring compounds (*left*) or simultaneously dehydrogenate and cyclize straight-chain hydrocarbons (*right*). In both examples the product is toluene, which has an octane number of more than 100. The octane number of methylcyclohexane is between 70 and 80. The octane number of *n*-heptane is zero. Reforming catalysts can also isomerize straight-chain hydrocarbons and crack large molecules into smaller ones.



FIRST STEP IN CATALYTIC DEHYDROGENATION is exemplified by the dissociative adsorption of molecular hydrogen on a catalytic surface. Each adsorbed hydrogen atom (H) may be bound to a single atom on the surface or it may be bound to two or more atoms.



ISOTOPIC EXCHANGE demonstrates that reacting species become dissociated on a catalytic surface. Here deuterium (D) and hydrogen (H) atoms trade places in methane (CH_4).



CATALYTIC SYNTHESIS OF AMMONIA is thought to involve dissociation of nitrogen and hydrogen (*1*) followed by addition of hydrogen to a complex consisting of nitrogen bound to atoms on the surface of the catalyst (*2, 3, 4*). Finally, ammonia (NH_3) is desorbed.

proceeds by means of the intermediate formation of a physisorbed species.

Step 3 usually involves one or mo elementary processes in which chemisorbed species react to form new chem sorbed species. In some cases step 3 ma involve reaction between a chemisorbed species and a molecule in the gas or liquid phase to form a new chemisorbed species. In step 4 the chemisorbed species desorbs, often by associative desorption, to give the final product.

Some simple cases may lack a surface-reaction step. Isotopic exchange between deuterium (the hydrogen isotope of mass two) and methane occurs on a number of transition metals (nickel and platinum) and their oxides. The reaction appears to proceed simply by dissociative adsorption followed by associative desorption [*see middle illustration at left*].

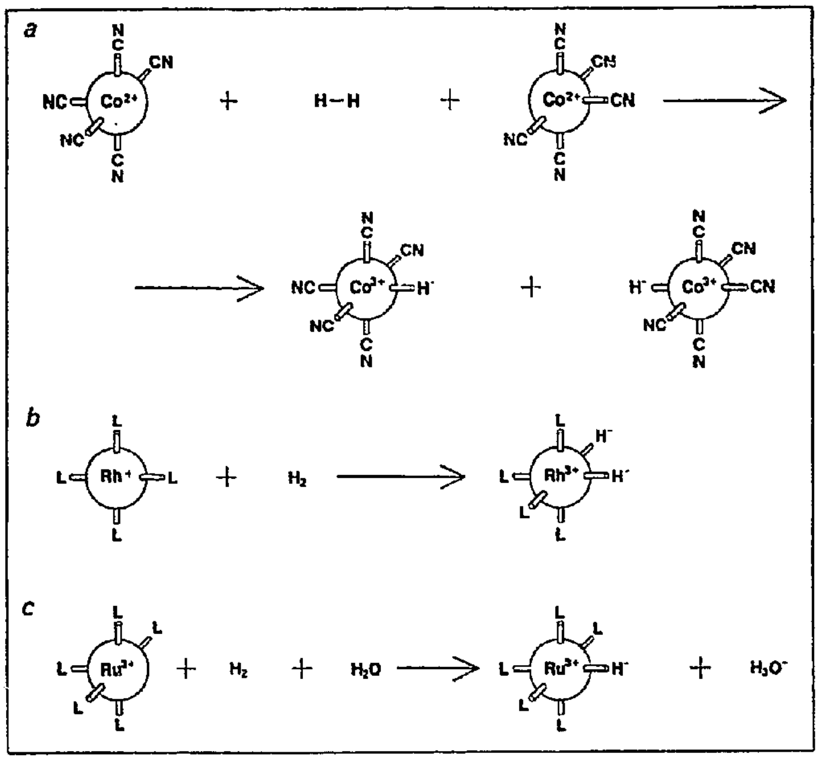
As Haber discovered, pure iron catalyzes the reaction of hydrogen with nitrogen to yield ammonia at about 450 degrees C. Presumably the first step in the process is that the hydrogen molecule (H_2) and the nitrogen molecule (N_2) are dissociatively adsorbed on the surface of the catalyst. Experimen with isotopes of nitrogen show that nitrogen does not dissociate at reasonabl rates on iron until the temperature ha been raised to about 450 degrees C. Hydrogen, on the other hand, dissociates freely even at the temperature of liquid nitrogen (−196 degrees C.).

It was suggested as long ago as the 1930's that the rate of ammonia synthesis is limited by the low rate of dissociation of nitrogen. It is hypothesized that once the nitrogen dissociates, forming a surface compound that can be designated N*Cat*, hydrogen atoms are added in three rapid steps forming HN*Cat*, H_2N*Cat* and finally H_3N*Cat*, from which NH_3 is readily released [*see bottom illustration at left*].

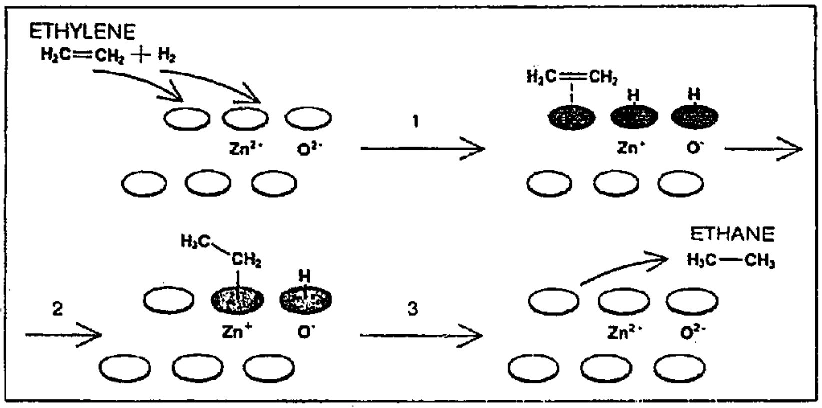
Subsequent work has supported and elaborated this mechanism, although many details are unclear and the intermediacy of an adsorbed molecule of nitrogen is favored by some. From the standpoint of industrial importance it has been found that iron plus a few percent of the oxides of potassium and aluminum, which are known as promoters, give a longer-lived catalyst and on with greater resistance to impuritie in the feed stream. Catalysts of this typ can often be used for several years.

The recently discovered reactions in which coordination complexes of transition elements function as homogeneous catalysts in adding hydrogen to various unsaturated compounds present close similarities to reactions effected by previously known heterogeneous hydrogenation catalysts. When transition elements are incorporated in organometallic compounds, they work as homogeneous catalysts capable of adding hydrogen to various unsaturated compounds. These active compounds are often coordination complexes. The complex must be "coordinatively" unsaturated if it is to activate hydrogen, that is, there must be a vacant or partially vacant position in the "coordination sphere" that surrounds the metal ion to which hydrogen can become bound. For example, cobalt pentacyanide [$Co(CN)_5$] has only five of six potential positions filled and can bind an atom of hydrogen in the empty position. A similar coordination complex can be formed with rhodium, which can hold two atoms of hydrogen in the same state of activation: H^-. The rhodium complex is oxidized by hydrogen to give a product in which the hydrogens are formally hydride ions. The reaction is called oxidative addition, and one can readily imagine an analogous oxidative dissociation adsorption. In coordination complexes incorporating ruthenium the hydrogen molecule is split into a positive state (H^+) and a negative state (H^-); the metal ion is not oxidized [*see upper illustration at right*].

The last process of activation is essentially the same as the one thought to operate on the surface of certain metal oxides that are used for hydrogenating olefins, for example zinc oxide (ZnO). In the case of ZnO the Zn^{2+} and O^{2-} act as coordinatively unsaturated surface species. (The superscripts refer to the number of electrons removed from or added to the dissociated fragment.) The zinc fragment binds hydrogen as H^- and the oxygen fragment binds hydrogen to form OH^-. The olefin is weakly adsorbed on a neighboring site and reacts in turn with the H^- and the hydrogen in the OH^-, thereby acquiring two hydrogen atoms [*see lower illustration at right*]. The process is called heterolytic dissociative adsorption to distinguish it from the homolytic adsorption of hydrogen on metals, in which the hydrogen molecule splits into two equally charged fragments.



COMPLEXES OF TRANSITION METALS, such as cobalt, rhodium and ruthenium, exhibit unusual catalytic properties. The complexes consist of ions of transition metals coordinated to side groups called ligands (*L*). Some complexes of this type are soluble in liquids and act as homogeneous catalysts. Pentacyanocobalt (*a*) is able to activate hydrogen because the "coordination sphere" around the cobalt ion (Co^{2+}) has an empty position that can hold a hydrogen ion that is formally in the negative state (H^-). The coordination sphere around the rhodium ion (*b*) can hold two hydrogen atoms, both H^-. In aqueous solution an organometallic compound of ruthenium (*c*) splits a molecule of hydrogen so that one fragment is negatively charged and one becomes bound to a molecule of water as a proton, forming H_3O^+. Catalysts of this type can produce the polymers shown on the next two pages.



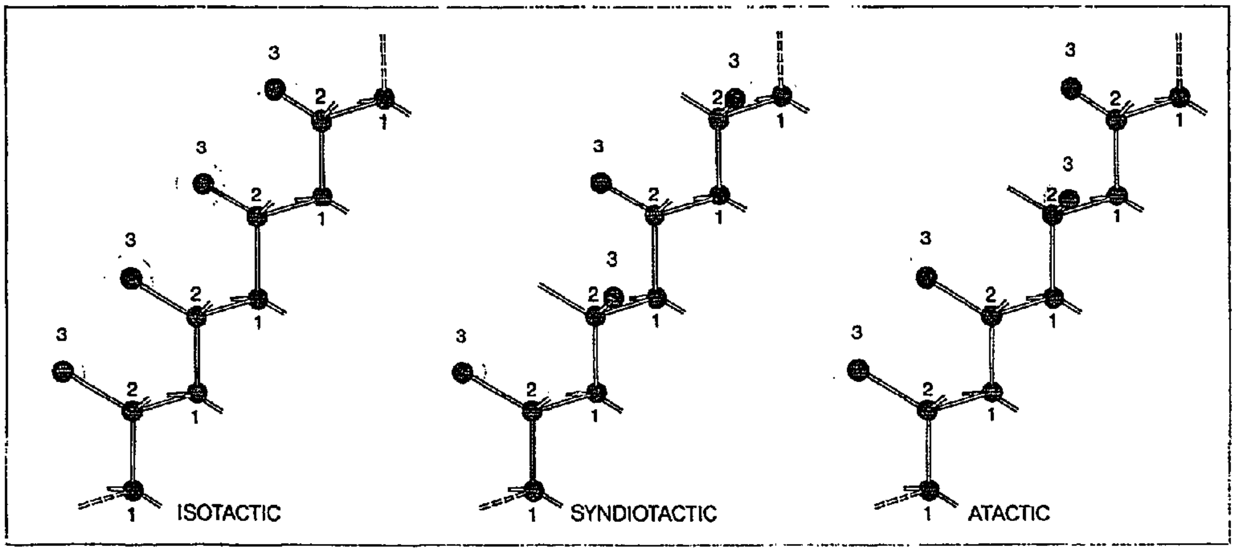
HYDROGENATION OF ETHYLENE, first achieved by Sabatier on a nickel catalyst, takes place readily on zinc oxide. The key sites appear to be coordinatively unsaturated metal ions (Zn^{2+}) and oxide ions (O^{2-}) on the surface. Ethylene ($H_2C:CH_2$) is adsorbed (*1*) and reacts in sequence (*2, 3*) with two hydrogen ions. The product is ethane ($H_3C \cdot CH_3$).

Mechanism of Hydrogenation

We have presented several examples of catalytic reactions and some of the current thinking about how they occur. Generally speaking, the mechanism of homogeneous catalysis is easier to elucidate than that of heterogeneous catalysis. In homogeneous catalysis elementary processes involve simple molecules and intermediates. In heterogeneous catalysis we must also consider the effect of surfaces. One cannot isolate a surface intermediate, recrystallize it and determine its structure by X-ray analysis. If surface reactions provide particularly useful possibilities for combinations of elementary processes, they also present special problems in the study of mechanism. We shall give several examples of the techniques that have proved to be helpful in that study.

Many of the extensively investigated

412



THREE KINDS OF POLYPROPYLENE can be made from propylene ($H_2C : CHCH_3$) with transition-metal catalysts. At a reaction temperature of 50 degrees C. a catalyst consisting of triethylaluminum and vanadium trichloride yields isotactic polypropylene, in which the methyl (CH_3) groups (*color*) all lie on the same side of the central chain of carbon atoms (*black balls*). Hydrogen atoms have been omitted; their locations are indicated by short bonds projecting from the carbon atoms. At a reaction temperature of —78 degrees C. a catalyst consisting of vanadium tetrachloride and diethyl aluminum chloride yields syndiotactic polypropylene, a molecule in which the methyl groups alternate from side to side. When the methyl groups project at random, the polymer is atactic.

reactions of heterogeneous catalysis are hydrogenations. We have discussed the hydrogenation of nitrogen to ammonia. Hydrogenations of organic compounds such as olefins, acetylenes (hydrocarbons with a triple bond between two adjacent carbon atoms) and ketones (compounds with a terminal oxygen atom doubly bonded to a carbon atom) are usually much easier and occur on a much wider variety of catalysts.

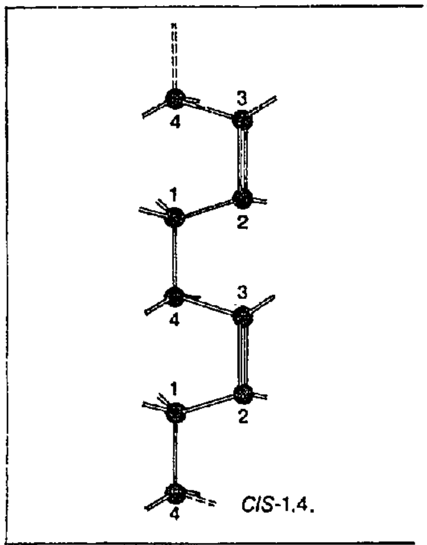
The hydrogenation of dimethylacetylene yields, depending on the catalyst, a number of interesting and useful products [*see top illustration on page 56*]. Dimethylacetylene (CH_3CCCH_3) is a chain of four carbon atoms with the central two carbons joined by a triple bond. If the hydrogenation is carried out at room temperature on nickel or platinum catalysts, the initial products are a mixture of butane (the fully saturated hydrocarbon C_4H_{10}) and two isomers of a four-carbon olefin: *trans*-2-butene and *cis*-2-butene, with *cis*-2-butene predominating. The designation "*trans*" means "located across from each other"; "*cis*" means "located on the same side." Here the terms refer to the location of the two methyl groups with respect to the double bond in the butene molecule.

On a palladium catalyst the initial product is almost exclusively *cis*-2-butene. In studying the mechanism of the reaction, chemists have used deuterium as the hydrogenating agent. By analyzing the product with the mass spectrograph one can separate the product into fractions that differ in the number of deuterium atoms incorporated in each butene molecule. By means of nuclear magnetic-resonance spectroscopy one can then determine the exact location in the molecule of the deuterium atom or atoms.

It turns out that as long as some dimethylacetylene remains unreacted, the initial product consists almost entirely of *cis*-2-butene bearing one deuterium atom on each of its two central carbon atoms. This is what one would expect if dimethylacetylene is chemically adsorbed on the surface of the catalyst by a breaking of one of the bonds between its central carbons [*see second illustration from top on page 56*].

Once all the dimethylacetylene has reacted, *cis*-2-butene begins to be hydrogenated to butane and isomerized to *trans*-2-butene. Actually isomerization is more rapid than hydrogenation. There is considerable evidence that the isomerization involves a mechanism first proposed by Juro Horiuchi and Michael Polanyi. Presumably as the *cis*-2-butene species is held to the catalyst by a single bond one of the two methyl groups rotates to an alternate position, after which a hydrogen replaces the catalytic bond and the molecule—now *trans*-2-butene—leaves the surface [*see third illustration from top on page 56*]. To account for the formation of still another isomer, 1-butene, one can postulate a mechanism that simply shifts the double bond in *cis*-2-butene from its location in the middle of the molecule to a new location between the first and second carbon atoms [*see bottom illustration on page 56*].

Studies with deuterium and a wide variety of hydrocarbons of different



FOUR POLYBUTADIENES, each precisely constructed, can be made from 1,3-butadiene ($H_2C : CHCH : CH_2$). The designation "1,3" indicates that the first and third carbon atoms in the molecule are joined to the next carbon in sequence by a double bond. If both double bonds open up and take part in structure have led to a rather good understanding of the nature of the intermediates formed in the reactions of hydrocarbons on metallic catalysts. Relatively little is known, however, about the nature of the chemical bond between metal and carbon, about the exact location of the adsorbed species on the surface of the catalyst and about the origin of the differences in behavior of different metals that act as catalysts.

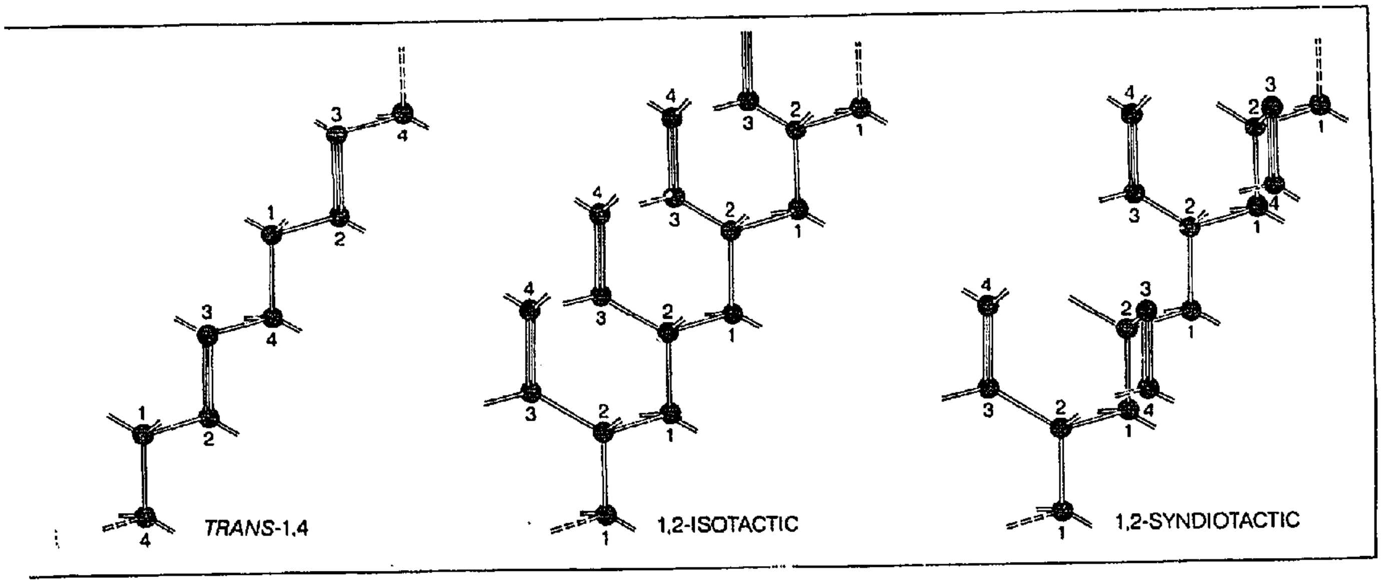
It will have been noted that all the arguments given above for the surface intermediates were inferential. One might hope to examine the catalyst during reaction by infrared spectroscopy and from the observed infrared spectra deduce what species are present on the surface. Some progress has in fact been made in such a program, but there is a difficulty. Much of the surface of most metals is occupied during hydrogenation by relatively slow-reacting species. That is, most of the surface species are not involved in the hydrogenation but the infrared spectroscope responds to the whole set of adsorbed species. It has not been easy to interpret the results.

More clear-cut results have been obtained with infrared spectroscopy of another type of hydrogenation catalyst, such as the zinc oxide catalyst mentioned above. Chromium oxide also acts as a hydrogenation catalyst. It appears that the key sites for activity on these oxides are coordinatively unsaturated metal ions and oxide ions at the surface. Heterolytic dissociative adsorption of hydrogen on these sites can be seen by infrared spectroscopy in the case of zinc oxide. The infrared studies indicate the presence of two kinds of adsorbed olefin. Ethylene is rather weakly adsorbed and then reacts with Zn^{2+}H^{-} [*see lower illustration on page 53*]. In contrast to the metals, the first reaction has no tendency to reverse. If one starts with ethylene (C$_2$H$_4$) and deuterium (D), the product is almost exclusively CH$_2$DCH$_2$D. For zinc oxide the deuterium studies provide fairly strong evidence for the illustrated mechanism and the infrared data add additional support. The isotopic distribution over metals is much more complicated.

Evidence from infrared spectroscopy and nuclear magnetic-resonance spectroscopy shows that simple olefins such as ethylene and propylene can be adsorbed on active surface sites in just about all the ways one might imagine. In some cases only a single carbon atom is bonded to the surface; in other cases two carbon atoms are bonded. Sometimes the double bond between the carbons is preserved; in other cases the double bond is opened and provides the link to the surface. It is apparent that quite an organometallic zoo can exist on the surface of metallic catalysts.

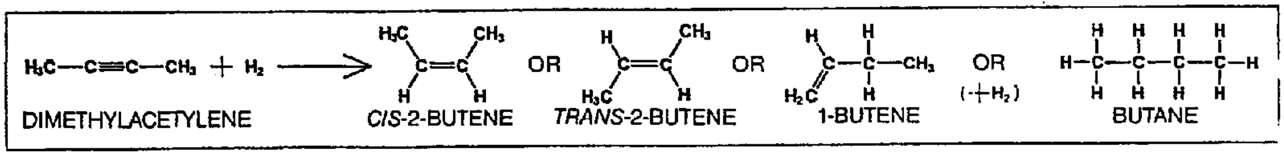
The practical aspects of catalysis involve the ability to perform a chemical reaction at a profit. In the simplest commercial installation the reagents and a catalyst are simply placed together in a vessel. The vessel is usually equipped with an indirect steam-heating system and a stirrer. When the reaction is completed, the vessel is emptied and the catalyst is separated from the product and may be reused in the next batch operation. In a continuous operation the reagents are preheated and pumped through a reactor containing the catalyst. The continuous type of operation provides for better control of conditions and ease of handling of product; it also allows operation at higher temperatures and pressures.

Ideally once the catalyst is placed in the reactor it should last indefinitely. In practice catalysts age, they become poisoned, they deteriorate physically and they accumulate reaction products or intermediates that undergo further reaction and finally deactivate the system. The whole idea in continuous operation is to maintain reasonably constant product quality. Usually as the catalyst deactivates, the temperature is raised to maintain a high yield. When these increases reach a limit, the catalyst may either be replaced or subjected to regeneration. For hydrocarbon reactions the regeneration means the removal of carbonaceous deposits. This is normally accomplished by passing a stream of gas with a controlled content of oxygen through the catalyst bed, thus burning off the deposits. While the catalyst is being regenerated or replaced, it is obvi-

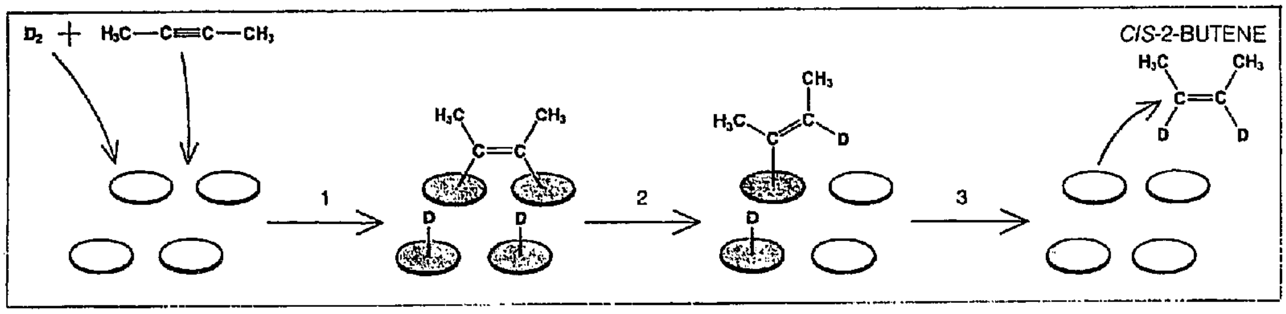


the polymerization, the resulting polymer consists of a continuous chain of carbon atoms with a double bond between every other pair of atoms. If the 1-2 and 3-4 single bonds both lie on the same side of the 2-3 double bond, the polymer is termed *cis*-1,4-polybutadiene. If the single bonds lie on opposite sides, the polymer is *trans*-1,4-polybutadiene. Here "1,4" indicates that the first and fourth carbon atoms in butadiene link up to form the polymer. If the polymerization involves only the double bond between the first and second carbons in each butadiene molecule, the third and fourth carbon atoms project as a side chain. If the side chains are all on one side of the central chain, the polymer is 1,2-isotactic polybutadiene. If the side chains alternate from side to side, the polymer is 1,2-syndiotactic polybutadiene. Each stereospecific configuration is produced by a distinctive transition-metal catalyst.

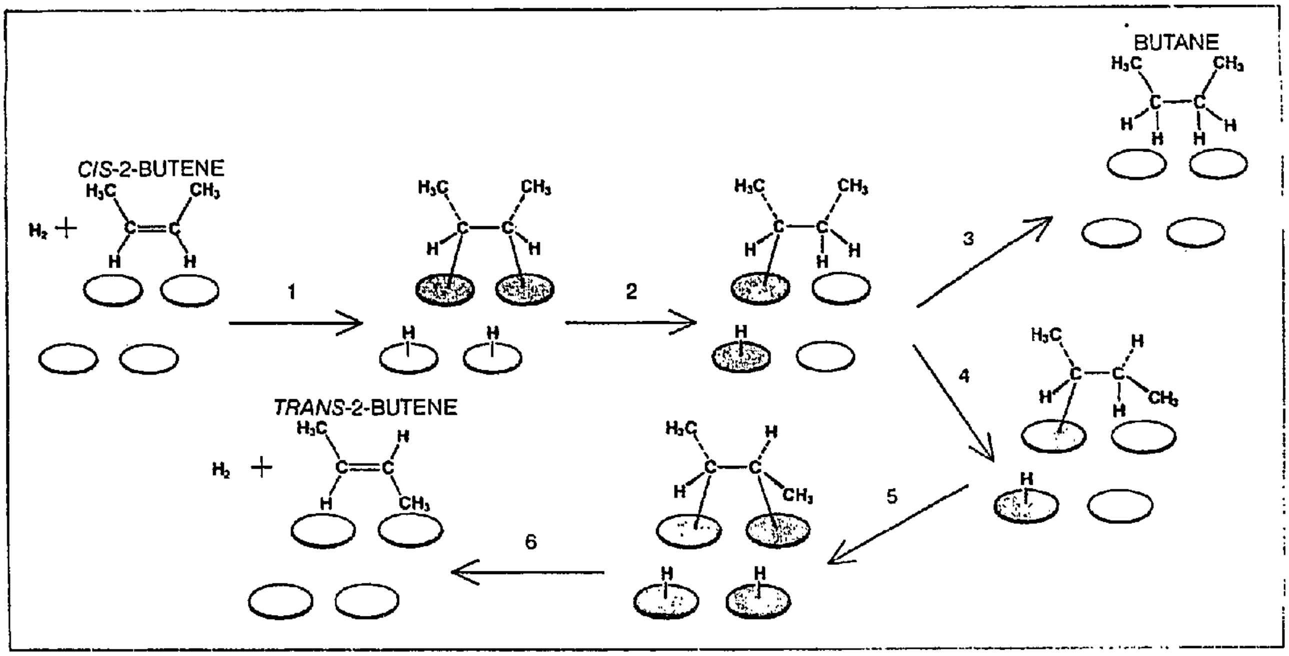
420



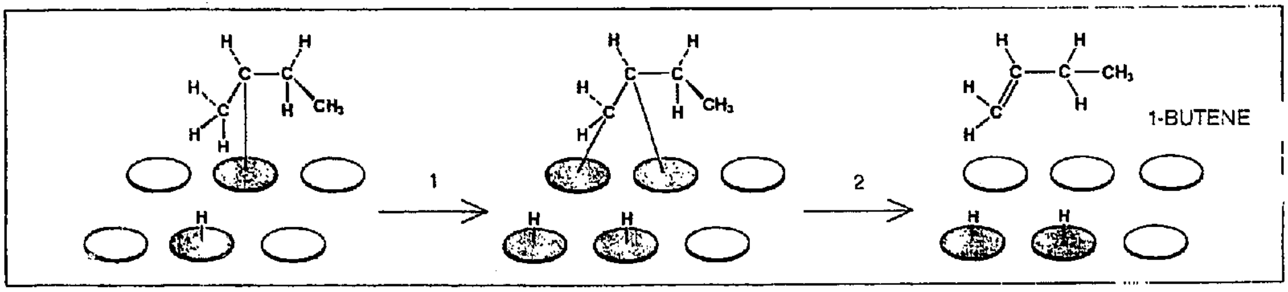
HYDROGENATION OF DIMETHYLACETYLENE can yield three different olefins, *cis*-2-butene, *trans*-2-butene and 1-butene, and the saturated hydrocarbon butane. With a palladium catalyst the initial product is chiefly *cis*-2-butene (*see mechanism below*).



MECHANISM OF HYDROGENATION of dimethylacetylene on palladium has been studied by substituting deuterium (D) for hydrogen. Dimethylacetylene is adsorbed to active sites (*color*) through its central carbon atoms (*1*). Two deuterium atoms are then added in sequence (*2, 3*), yielding *cis*-2-butene. "*Cis*" indicates that the two methyl groups are on the same side of the double bond.



FURTHER HYDROGENATION AND ISOMERIZATION of *cis*-2-butene can occur once all the dimethylacetylene has reacted. *Cis*-2-butene is presumably readsorbed and can acquire two more hydrogens (*2, 3*) to form butane. Alternatively one methyl group can rotate to a new position (*4*). The hydrocarbon again forms a double bond with the palladium (*5*) and emerges as *trans*-2-butene (*6*).



FURTHER ISOMERIZATION converts *trans*-2-butene to 1-butene. The *trans* molecule is evidently readsorbed so that its first and second carbon atoms are linked to active sites (*1*). On desorption (*2*) the double bond appears between the first and the second carbon.

ously not making product; ideally, if one has to regenerate, one would prefer to do it continuously and not interfere with the processing of the raw material.

An excellent example of continuous processing and regeneration is the catalytic cracking of oils [*see illustration on next page*]. The catalyst, in finely divided form, is carried into the reactor by the upward flow of vaporized oil, the catalyst-product mixture is withdrawn from the top of the reactor and the catalyst is inertially removed from the product vapors in a cyclone separator. The catalyst is then stripped with steam to remove entrained product and is fed by gravity into a regeneration vessel where it comes in contact with a countercurrent stream of air that burns off the carbonaceous deposits. The clean, hot catalyst is fed through a standpipe and is picked up by the incoming fresh oil. The circulation of catalyst through the reactor and regenerator is very large with respect to the oil processed. Currently more than 6.9 million barrels of oil per day are subjected to catalytic cracking. The catalyst circulation on a daily basis amounts to eight million tons. About .15 pound of catalyst per barrel of oil is added to the unit in order to compensate for loss and withdrawal, thus allowing for the maintenance of equilibrium activity.

Catalysts are prepared in many different ways. A catalyst widely used in catalytic cracking is a composite of silica (SiO_2) and alumina (Al_2O_3), which can be prepared by neutralizing a solution of water glass (Na_2SiO_3) with sulfuric acid to form a gelatinous precipitate that is a polymerized silicic acid [$(H_2SiO_3 \times H_2O)_n$]. This is next treated with aluminum sulfate solution [$Al_2(SO_4)_3$] and ammonia to precipitate aluminum hydroxide [$Al(OH)_3$] on the silicic acid precipitate. The composite is filtered and thoroughly washed to remove all soluble salts. It is then dried in air and calcined at about 500 degrees C. The resulting material contains about 75 percent SiO_2 and 25 percent Al_2O_3 by weight and is believed to have a structure wherein trivalent aluminum atoms are incorporated within a tetrahedral matrix of polymeric silicic acid. Each trivalent aluminum atom thus has to carry a net positive charge to compensate for its enforced tetrahedral coordination.

These positive, or electron-deficient, sites serve as the locus of acidity; in fact, the strength of the acidity thereby created is comparable to the strength of mineral acids such as sulfuric acid. Unlike most mineral acids, the acids created are very stable at high temperatures. The total number of sites is limited and is related to the surface area of the composite. The usual surface area for fresh silica-alumina is about 600 square meters per gram of catalyst. This remarkable surface area is due to a multitude of extremely small channels ranging from five to 100 angstroms in diameter. In service some of the smaller channels collapse, and there is a substantial loss in surface area: down to about 150 square meters per gram. The larger channels survive, however, and the acidity function in these channels is retained.

In general at a given temperature the reaction rate on a heterogeneous catalyst is dependent on two factors: the number of active sites available to the reactant and the turnover rate. The number of active sites is related to the surface area, whereas the turnover rate is a function of the chemistry of the site in relation to the reactant. If the chemistry of the site is such that a reactant stays too long on a site, and during that time is not available to another reactant molecule, the turnover number is low.

Catalytic Reforming

We have pointed out that the gasoline fraction, or virgin naphtha, obtained from crude oil by fractionation needs upgrading to be useful as a motor fuel. Since about 1930 there has been a continuing need to increase the octane number of gasoline. In 1930 the average gasoline had an octane number of about 65; today the average is about 100. To meet this demand new catalytic processes have had to be developed and widely employed.

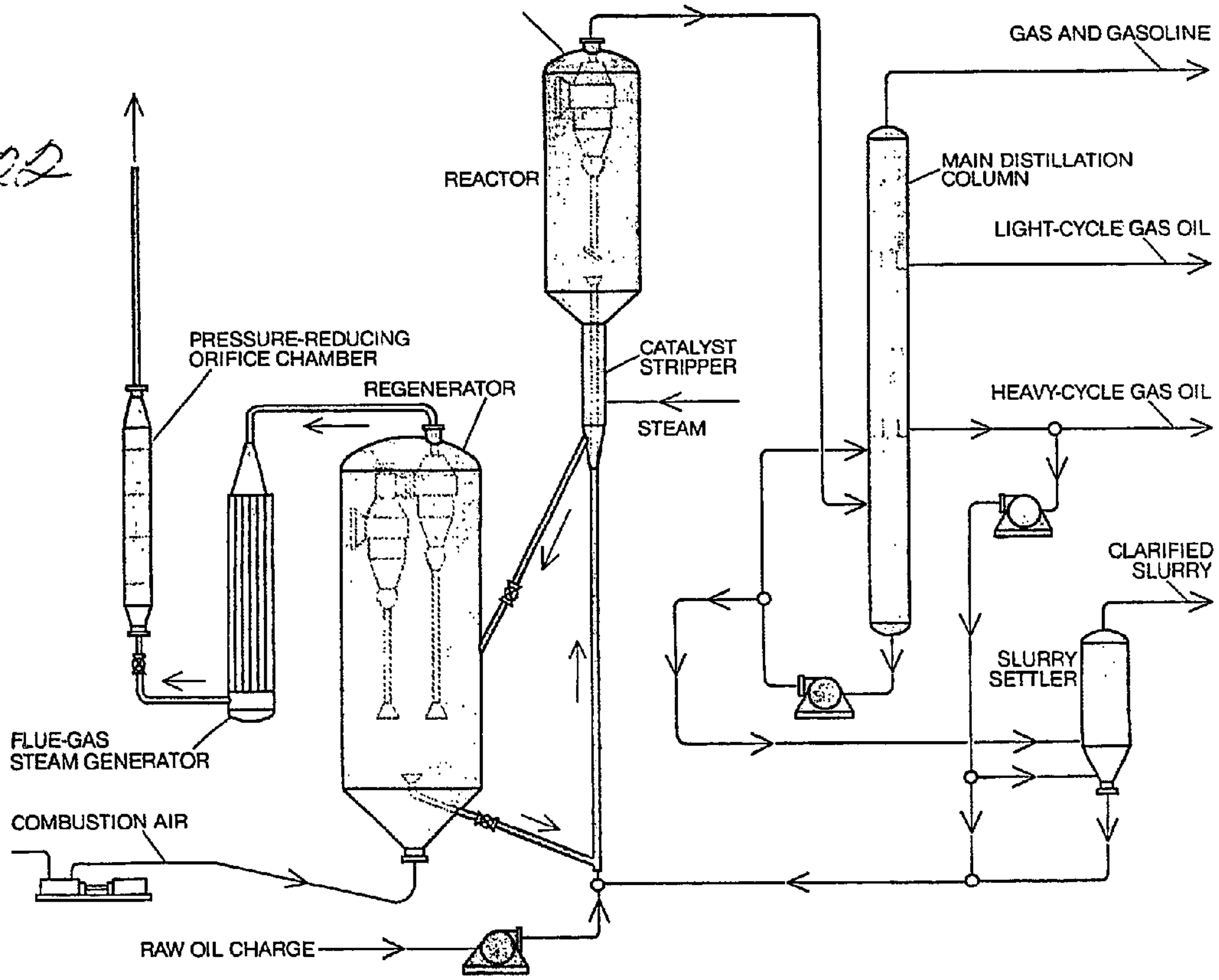
During the 1950's new platinum-alumina-halogen catalysts were introduced to carry out the catalytic reforming of low-octane oil fractions. The new catalysts performed a dual function by maintaining a proper balance between two catalytic requirements. In general the reactions of catalytic reforming require two types of sites: hydrogenation-dehydrogenation sites (provided by platinum) and acidic sites; catalytic reforming does not occur in the absence of either. The main advantages of the use of this type of catalyst are considerably higher selectivity (higher yield), higher octane number and the ability to run continuously without frequent regeneration.

The chemistry of catalytic reforming using platinum catalysts involves four major reactions. The first is the dehydrogenation of cyclic hydrocarbons, for example converting methylcyclohexane into toluene. The second is dehydrocyclization of paraffins (saturated open-chain hydrocarbons), for example converting normal heptane into toluene [*see bottom illustration on page 51*]. The third is hydrocracking, which means breaking long-chain paraffins into two smaller molecules and adding hydrogen at the sites where the original chain has been broken. The fourth is isomerization, which means converting a straight-chain hydrocarbon into a branched-chain molecule.

All these reactions lead to an octane-number enhancement. For example, the second reaction converts normal heptane, with an octane number of zero, to toluene, which has an octane number in excess of 100. The third reaction can convert decane, for example, with an octane rating of less than zero, into two molecules of isopentane with an octane number of 90. The first and second reactions are strongly endothermic; the third is exothermic; the fourth is essentially thermoneutral. To maintain an overall heat balance one must use multiple reactors with intermediate reheating. Although the overall system produces hydrogen, the process is carried out in the presence of excess hydrogen (recycled from the first and second reactions) at pressures ranging from 150 to 500 pounds per square inch. The excess hydrogen holds down the deposition of carbonaceous material on the catalyst. By this expedient a catalyst can be used continuously for as long as three years. Reaction temperatures are held between 475 and 550 degrees C. Between one volume and three volumes of gasoline are processed per volume of catalyst per hour. The catalyst contains between .3 and .8 percent platinum and up to about 1 percent chlorine or fluorine on a base of highly porous alumina. During the lifetime of the catalyst each platinum atom leads to the reaction of some 20 million molecules of gasoline, a truly catalytic act. The function of the halogen is to induce acid reactions, which convert saturated hydrocarbon rings into benzene (unsaturated) rings.

The formation of benzene-ring, or aromatic, compounds from paraffins (dehydrocyclization) is extremely complex. Some 10 to 15 intermediate steps are postulated. They require the presence of both platinum and acid sites, and adsorbed hydrocarbons evidently migrate from one site to another. In spite of this complexity the efficiency of conversion from the paraffin to an equilibrium mixture of aromatics is of the order of 90 percent. Even higher efficiencies are obtained with the newly developed platinum-rhenium-halogen-alumina catalysts. Since its introduction in 1949, catalytic reforming, using dual-function plati-

422



FLUID CATALYTIC CRACKING PROCESS was developed in the late 1930's. The catalyst is in the form of fine grains that behave in the reactor much like a fluid when agitated from below by vaporized oil. The large object depicted in gray inside the reactor is a cyclone separator that removes the catalyst from the reactor product. The reactor product passes to a distillation column where fractions of different volatility are separated. Part of the heaviest fraction is recycled to the reactor. A portion of the catalyst is continuously transferred by gravity from the reactor to the regenerator, where it again behaves like a fluid when it is subjected to a flow of air that burns off carbonaceous deposits. The reactivated catalyst is returned continuously to the reactor. The hot air leaving the regenerator is used to make steam. The catalytic cracker illustrated here was designed by the Universal Oil Products Company.

num-containing catalysts, has grown in importance. Today some 6.8 million barrels per day are processed by this catalytic system in the U.S., western Europe and Japan.

The Future of Catalysis

Although it has attained tremendous practical importance, heterogeneous catalysis has attracted few workers in the chemistry departments of American universities. One may suspect that the need for new areas of research will one day lead organic chemists to extend their interest to heterogeneous catalysis, but only a handful have taken the step so far. In recent years, however, a number of aspects of heterogeneous catalysis have received increased attention in American departments of chemical engineering. There are several other countries where the number of university chemists interested in heterogeneous catalysis is relatively large: Japan, the Netherlands and the U.S.S.R. in particular. It will be interesting to see if this university activity is followed by important technological developments.

One must admit that in spite of the considerable progress in the technological and scientific aspects of catalysis, only experiment can establish whether or not a specific chemical material will make a suitable catalyst for a particular reaction. For many thermodynamically possible reactions no catalysts are known, and many of the catalysts we know were discovered by accident or by a very extensive screening program. The discovery of new promoters has been little helped by theory. The added complexity of the surface makes heterogeneous catalysis an interdisciplinary subject. Both surface chemistry and surface physics must, so to speak, precede heterogeneous catalysis. Therefore a better understanding of many aspects of heterogeneous catalysis must await further advances in the chemistry and physics of surfaces.

New tools are being developed that will enable us to look more closely at the surface of the catalyst and thus possibly gain some additional understanding. The interdisciplinary nature of the study of catalysis, involving as it does both surface chemistry and surface physics, will also require close cooperation with other sciences.

APPENDIX B

from Reactivity of Solids, Proceedings of the Seventh Internationa Symposium on the Reactivity of Solids, Bristol, 17-21 July, 1972, published by Chapman & Hall Ltd.

from Plenary Lecture "Recent Approaches to the Interpretation of Atom-Surface Interactions, by T.N.Rhodin, School of Applied and Engineering Physics, Cornell University, Ithaca, New York, 14850.

SURFACE ANALYSIS METHODS

← MEASURED →

↑ INCIDENT ↓

	R+μ	IR	OPT	UV	XR	γ	LEE	HEE	IONS
RADIO & MICROWAVES	NMR ESR	–	–	–	–	–	–	–	–
INFRARED		EM. & SCATT.	–	–	–	–	–	–	–
OPTICAL			ELL.	–	–	–	PES	–	PD
ULTRAVIOLET					–	–	UPS	–	
X-RAYS					XRF	–	XPS		
GAMMA RAYS						MÖSS.			
LOW ENERGY ELECTRONS				UVE	APS		(LEED) ILEED AES IS	–	ED
HIGH ENERGY ELECTRONS					EEX			(HEED)	
LIGHT IONS					IEX		INS		ISS (FIM)
HEAVY IONS									IMA
SPARK, ARC			EM. SP.		–	–		–	MASS SP.
$\vec{E}$ FIELD	–	–	–	–	–	–	FES	–	FD

APPLICABILITY OF METHODS VARIES WITH MATERIAL TYPE

Fig. 9 Tabulation of surface analysis methods in terms of the incident excitation and the measured emission. .(after Nagel (38))

R + μ = resonance
IR = infra-red
OPT = optical
UV = ultraviolet
XR = x-ray (ESCA)
γ = gamma ray
LEE = low energy electron
HEE = high energy electron
NMR = nuclear magnetic resonance
ESR = electron spin resonance
EM = emission
SCATT = scattering
ELL = ellipsometry
EM SP = emission spectroscopy
UVE = ultraviolet emission
XRF = x-ray fluorescence
APS = appearance potential spectroscopy
EEX = electron-excited x-rays
IEX = ion-excited x-rays
MÖSS = Mössbauer spectroscopy

PES = photoemission spectroscopy
UPS = ultraviolet photoemission spectroscopy
XPS = x-ray photoemission spectroscopy
AES = Auger electron spectroscopy
IS = ionization spectroscopy
INS = ion neutralization spectroscopy
FES = field emission spectroscopy
PH = photo desorption
ED = electron desorption
ISS = ion scattering spectroscopy
FIM = field ion microscope
IMA = ion microprobe analyzer
MASS SP = mass spectroscopy
FD = field desorption

APPENDIX C

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APPENDIX D

RESEARCH RECOMMENDATIONS

Gabor Somorjai
University of California Berkeley

1. Research for new Catalysis for hydrogenation of coal.
2. Research for Catalytic nitrogen fixation and catalytic decomposition of NO, according to $2\ NO \rightleftarrows N_2+O_2$.
3. Research on catalytic dissociation of water according to $2\ H_2O \rightleftarrows 2\ H_2+O_2$.
4. Research to find catalysts to replace platinum and platinum group metals.

RECOMMENDATIONS

Heinz Heinemann
Mobil Research and Development Corporation

I would like to add to the recommendations, a point that was made during the discussions. It has to do with the importance of examining identical catalyst samples with various tools and for different catalytic reactions. A large portion of the voluminous data available in the literature is difficult if not impossible to extrapolate because various investigators have worked with similar catalysts of different origin and prepared by different methods. Anyone in the field of catalysis is aware of the great differences in activity and selectivity that can be caused by differences in catalyst preparation techniques.

A better understanding of catalytic mechanisms and the ability to make predictions would be greatly enhanced by having information obtained using tools and different chemical reactions on the identical catalyst sample.

ADDITIONAL RECOMMENDATIONS: A TIME TABLE

James T. Richardson
University of Houston

Time	Action
Immediate	• Conservation of energy • Relaxation of pollution standards
Next 3-5 years	• Increased oil and gas production • More efficient petroleum refining operations • More efficient energy conversion devices • Improved pollution control • Exploratory research into alternate energy sources • Increased nuclear plants
5-10 years	• Coal gasification and liquifaction • Vastly improved power conversion cycles, stationary and moving
10 + years	• Increased large scale use of solar, geothermal, nuclear energy • Alternate automotive fuels, e.g. methanol • Fuel cells
20 + years	• hydrogen (non-fossil derived) energy carriers • MHD • Synthetic (coal based) chemical industry

All this together with a change of life style for us all. We are all agreed that catalysis will play an expanded role in this evolution. Distinct areas of catalytic activity are evident.

(1) Improved petroleum conversion (From crude to environment). These include improvements in existing refining operations such as

- hydrodesulfurization
- catalytic cracking
- catalytic reforming

covering the whole spectrum of petroleum products.

Also included are

- stack-gas clean-up
- product purification

Most of these improvements are already in progress. Industrial research, based on current knowledge, is in the best position to quickly and efficiently bring these factors into play.

(2) Coal catalysis

There are two areas:

a) Catalysts for gasification and liquefaction.

The current situation is completely unsatisfactory. Most applications will be very expensive or operationally impossible. I am convinced that we shall need new chemistry for this problem. There is much fruitful research here of a long-range nature. For instance - how can we turn the coal (or the mineral matter) itself into our catalyst. Here is the place for visionary attitudes.

b) Coal gas conversion via

- methanol synthesis
- methanation
- Fischer-Tropsch synthesis

There is much existing research and technology in all these processes. But much remains to be done before we have optimized the efficiency, stability and poison resistance of the catalysts. Also the many types of hydrocarbons derived from the Fischer-Tropsch synthesis offers a challenge in catalyst selectivity control.

(3) Improved power conversion

Fuel cells will undoubtedly be important and efficient electrode catalysis will assume new dimensions. But the possibility of catalytic conversions during conventional power cycles should be explored. It may be possible to attain higher turbine temperatures through utilization of exothermic reactions in the gas. There are many such fruitful areas for improved efficiency through catalysis.

(4) Catalysis and new energy

Here the challenge is hydrogen production. The efficiency of direct decomposition of water over electrolysis is so advantageous that this route must be explored. The non-fossil energy sources - nuclear and solar - do not provide high enough temperatures. To circumvent this, elaborate chemical cycles have been devised. Perhaps catalysis (e.g. photocatalysis via solar energy) is the answer. Much research needs to be done.

We should be concerned with the development of pathways that will open up (2), (3) and (4) above.

As far as DOD is concerned, the promotion of these aims will be of interest. But there must be many obvious applications waiting for exploitation. The self-sufficient aircraft carrier is one example. Perhaps a panel of catalyst experts would be of value to DOD in discovering others. It would certainly be a most interesting assignment.