CATALYSIS FOR PRODUCTION OF GASEOUS FUELS FROM LIQUID HYDROCARBONS

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I want to discuss a new American industry, making nice clean gas from nice clean liquids. You might ask, "Why do it?". The answer is our economy is geared to the use of natural gas. As long as we have burners that require natural gas, industries that feed on it and pipelines that need it, the gas companies are going to look for ways to supply it. Let's look at the projection of our need for natural gas. The projections in slide number 1 are taken from Shell Oil Company information.

At present, one third of our energy consumption is provided by natural gas, promoted by its availability and low price, which has been artificial. Over the next five years there will be little change in demand for natural gas. The Shell projections in slide number 2 show a peak about 1972 in the availability of "natural" natural gas, NNG. From now on we need some other source to supplement the imported LNG, such as SNG from oil and coal gasification.

At the present time, the gas industry is depending heavily upon the catalytic gasification of oil to SNG. This is a stop gap measure. I doubt if these figures are realistic, because there is a feed stock problem which will promote the production of gas from coal. When the gas industry realized the situation two or three years ago, there was a frantic rush for processes which would produce gas and for feed stocks. It was disconcerting to realize that there was no American commercial process that would fill the need.

The next slide shows the various process routes we have. We can cover the whole range from the LPG and the natural gas liquids and the light virgin naphthas, the crude oil and also the heavy distillates of the crude oil, all the way down. Very few processes are commercially proven for the SNG requirements in the United States. They all have their problems. The one that attracted most attention was the low temperature catalytic steam reforming process for making synthetic natural gas from naphtha and these natural gas liquids. Recently we've also been interested in combining this process with a hydrocracking of crude oil, to use cracked naphtha. This type of plant is easily built and quickly. The capital investment is modest. There are problems of import permits and domestic supply, and from a catalytic point of view, the deposition of carbon.

The next slide, number 3, shows available processes from various manufacturers, all foreign with the exception of partial oxidation. There is a very good reason for this; we were not interested in making gas ten years ago, but the British, Germans and the Japanese were. They were making town gas. It takes very little processing to upgrade town gas into a synthetic natural gas. All of the plants currently under design or construction in the United States are based on one of three catalytic processes, all very similar. They vary in some aspects in the composition of the catalyst, but they all, essentially, do the same things, although the economics are different.

The process for the naphtha steam reforming is shown in the next slide. Virgin naphtha first goes through a hydrodesulfurization treatment, which requires hydrogen. This is necessary because catalysts used are very sensitive to sulfur and the sulfur level must be less than one part per million (ppm), depending on the process used. The naphtha is then passed through the gasification stage, mixed with steam, and reacted to give an equilibrium mixture of methane, carbon oxides, hydrogen, and water. This is the same process used in Europe and Japan for two gas. Product gas is then methanated to remove the hydrogen and the CO, although this methanation is not nearly as severe as the methanation encountered in coal gasification. This technology has been proven with no problems.

The next slide, number 5, which shows the number of plants completed, is about six months old, so these figures may not be accurate. Seven plants are under construction. Two of these are now on stream. Twenty-four are in the engineering and planning stage, so there are 30 to 40 plants under design. I think we'll see these seven plants completed but I have doubths about the others because of unavailability of naphtha. The next slide, number 6, shows the location of the plants, mostly in the east and the mid-west.

Another route, the direct refining of crude oil, is shown in the next slide, number 7. In the proposed energy refinery crude oil is fractionated, goes through hydrodesulfurization and conventional hydrocracking. Hydrocracked naphtha is gasified to SNG, with fuel oil as the other product. SNG and fuel oil are mixed as the market demands. Economics of such a refinery clearly show no major capital investment to be in naphtha preparation. If steam reforming could be upgraded to handle heavier fractions, overall savings would result from decreased, upstream processing. Thus it is important to improve the performance of the catalyst for this service.

The next slide, number 8, shows the number of contemplated energy refineries, and number 9 shows their location.

The chemistry of this process is well established as follows in slide number 10. First, the gasification reaction, steam and naphtha to make CO and hydrogen, together with direct hydrogenolysis. Next are the shift and the methanation reactions which are very fast under these conditions and reach equilibrium. All the naphtha is consumed to an equilibrium mixture of the carbon oxides, methane, hydrogen, and steam. Very little is known about the mechanism of this reaction. We don't even know the kinetics very well, but the catalyst must adsorb and dissociate the hydrocarbon to form CH_x fragments on the metallic surface. These react with steam, either directly from the gas phase or with steam that has been adsorbed on the support and migrates to the metal. So the catalyst must activate the fragmentation of these hydrocarbons and the adsorption of steam. It is desirable to have gasification and the hydrogenolysis proceeding simultaneously, although hydrogenolysis could have bad effects since it also results in the formation of coke.

The reaction goes to equilibrium so the process conditions are determined by thermodynamics. The next slide, number 11, shows the product distribution as a function of temperature which is the most sensitive parameter, the others being pressure, and steam-to-hydrocarbon ratio. At high temperatures, equilibrium favors the production of hydrogen. This is the region for synthesis gas manufacture as in the conventional steam reforming. Town gases, used in Europe, form at intermediate temperatures. This 500 to 600 BTU/cu. ft. gas was a substitute after the European gas industry switched from coal to oil. Europe is now changing from manufactured town gas to natural gas.

The lower temperatures favor the production of methane. After methanation, CO_2 removal and drying, the gas is 98% methane, has approximately 1,000 BTU/cu ft. and is comparable to natural gas.

There are, however, differences between European and American usage which must be kept in mind. In the European markets, these plants are peak-saving, and operate only during the winter. They are small plants and use light feed stock. In the United States the plants will be very large, as much as 500 million cu. ft. per day. They will operate as base-load plants continuously and will have an increasing demand for more flexible feed stock higher boiling point naphthas. The key is then dependability and long life. The catalyst requirements shown in slide number 12 are clearly defined. The SNG process needs a high activity catalyst for a wide range of naphtha compositions, with long life under a full load continuous operation. These are achieved in available commercial catalysts. The next slide, number 13, shows the key features; an active component, (nickel has been found to be the cheapest most active component), a large surface area, (we would like to have a high effectiveness factor, this is not always controllable, since these processes are diffusion limited), long life, low sintering rates, low accumulation of coke and resistance to sulfur. The problems encountered in this process points out the need for more research in each of these important deactivation mechanisms. Accumulation of coke is the most important, sintering is next, followed by resistance to sulfur. In methanation of coal gas, the emphasis is in a different order. Sintering, sulfur poisoning and coking, in that order.

Commercial catalysts shown on the next slide, number 14, were developed from catalysts available for other needs. There has been some improvement and modification in the last few years, but not much. The nickel content is from 30 to 75 weight percent, with a nickel surface area of 30 to 50 square meters per gram. Silicates, silica and alumina, are used as supports; all methods are used for preparation. Different types of promoters are found; potassium on an alumina support is quite helpful in neutralizing some of the acidic sites on the alumina to cut down the coking and also to act as a catalyst for the removal of coke with steam. Magnesium is important in stabilizing the nickel surface area and decreasing the rate of sintering. One manufacturer adds copper chromite to the catalyst to remove the sulfur before it poisons the nickel. These catalysts are all in production and working. We will see some modifications and some improvements in the years ahead as summarized on the last slide, number 15.

There will be changes to reduce coking, allowing higher boiling feeds with less steam. Less sintering will add a longer life to the catalyst. Higher activity is not necessary, but would be useful since we could either operate at lower temperatures with higher methane yields, or use the higher boiling feeds. We could also cut down on the size of the units. I don't think we're going to have major changes in the overall catalytic composition or formulation unless there are radical changes in the process, e.g., from fixed to fluidized beds. I don't think this will happen as long as there is the current unstable situation with the supply of naphtha and with coal gasification coming into the picture.

Discussion

Klimisch: Carbon is an equilibrium product and you have a lower temperature, have you taken that into account?

Richardson: Carbon on the catalyst?

Klimisch: To assist the equilibrium production, it becomesimportant at the lower temperature.

Richardson: Not under these conditions with steam.

Klimisch: We've done some recent calculations that seem to show that.

Richardson: No. I don't think the experience on the pilot unit or in the laboratory has demonstrated any real problems with the carbon depositions. Although these catalysts do coke, they stay fairly clean. The steam ratio is maintained high enough to do this.

Hightower: It depends on the form of the carbon, I think, as to what thermodynamic value - you looked these up in tables, I guess.

Klimisch: We used the NASA program which does take into account solids. Carbon shows up at lower temperatures.

Richardson: Perhaps, you should look at the nickel-carbon system.

Rabo: The NASA program has one problem. It considers carbon as graphite.

Mills: Okagama gave a very interesting talk last Wednesday, in which he had the carbon on the catalyst much different from graphite.

Emmett: I question the difference between graphite and carbon on the catalyst. We made equilibrium measurements on the carbon supported on nickel and it is equal to graphite within about 212 calories. I don't know the paper to which you refer.

Emmett: From the synthetic-gas plants, what's the total gas production compared to our natural gas usage - 1%?

Richardson: I'm sorry, I don't remember the numbers; it's a small fraction, not a large amount, but if you don't have that small fraction coming into your home, you're angry.

Lauriete: I was curious why you catalyst experts have never used electro-sieves as support structures? Since your interests involve the surface, it would seem logical that you would coat the sieves with catalyst.

Heinemann: There are very few molecular sieves that are stable at these conditions of temperature and steam.

Lauriete: You don't have to metallize at steam temperature; you can metallize at room temperature.

Haensel: That leads to very inactive systems.

Hightower: Vapor deposition of the metal, is that right?

Haensel: Yes.

<u>Richardson:</u> The surface area of the support may not be so important after the catalysis reaches some kind of a steady state. The stabilizers that are added after the precipitation or impregnation are more important. Most of the commercial catalysts have roughly the same type of surface area.

<u>Bailey</u>: You remarked about there being a heat balance overall for your set of reactions. Unfortunately, however, the one which is highly endothermic is the one occurring at the very high temperature. The one which is exothermic is the one which is favored at the low temperature. You remarked about the possibility of doing it all in one stage. So far as I know, that has not been achieved as yet. It would be very desirable because of feed balance; is that correct?

<u>Richardson</u>: I don't think I said anything about the heat balance.

<u>Bailey</u>: I misunderstood you then. Certainly, you're much nearer heat balance if you could do it all in one stage because reaction one, the gasification, is highly endothermic and must occur at high temperatures. The exothermic reaction, namely methanation, is favored at lower temperatures. So, without a single system in which they all occur together you have the problem that the heat that's given up is given out at a lower temperature, the heat that's required is required at a high temperature.

<u>Richardson</u>: These processes run adiabatically. The first reaction that takes place is the endothermic gasification. The temperature drops. Methanation takes over, the temperature comes up, reaches an equilibrium value, so that there is a well-defined temperature profile in the bed that is a powerful indicator, not only of the kinetics of the reaction, but also of the deactivation mechanism.

Bailey: Can you run the whole set in one single closed system?

Richardson: Yes.

Hall: In our energy short economy, in which we aim to become self sufficient by utilizing coal as Dr. Bailey has suggested, what's the rational for converting naphtha, which we need for automotive transportation, into methane. Why isn't making methane from coal more rational?

Richardson: The rationale was that the gas companies, three years ago, thought they could get the naphtha and the process was available to them. They could have plants operating in 1973, which they have done. The situation is now changed.

Hall: So, the main thing is to keep these plants operating and not to build any more?

Richardson: I think that's what's going to happen.

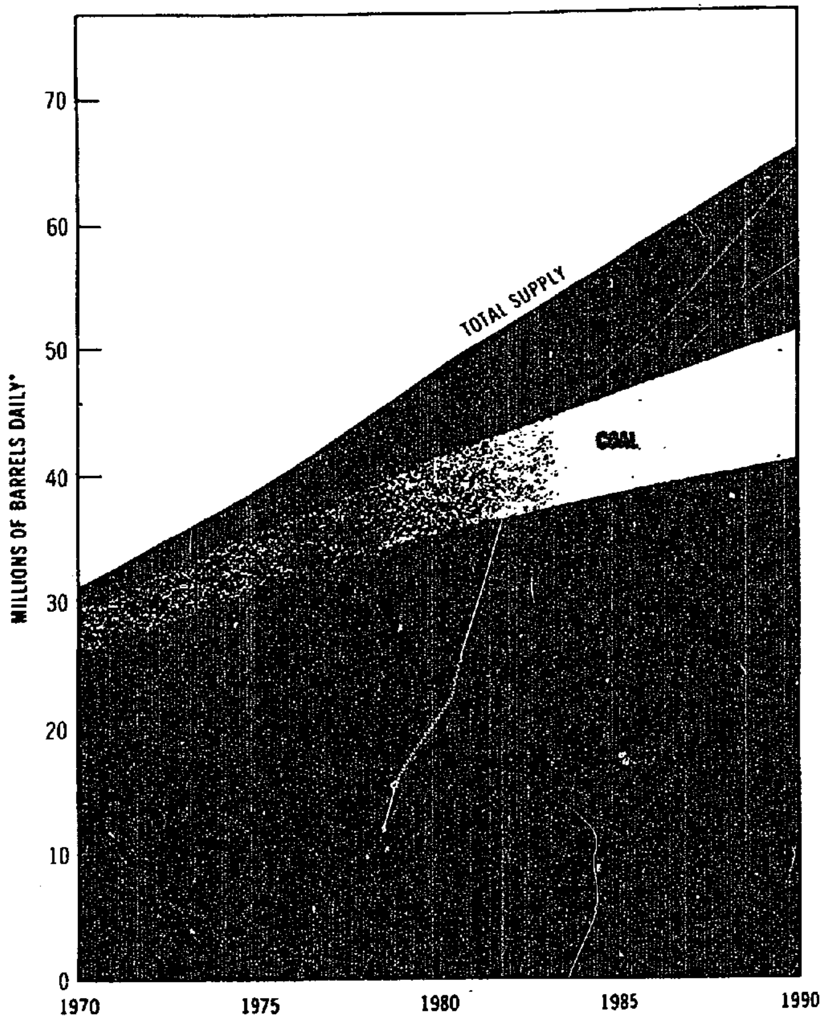
Lindquist: Joe Moore, Bonner and Moore, at the Fifth Synthetic Pipeline and Gas Conference last week, said that all 34 plants could be supported by naphtha from the European refineries where the naphtha is in excess because Europe does not have the requirement for naphtha that we have, so felt that naphtha would be available for all 34 plants at a cost of about 130% of crude.

Bailey: Naphtha availability from European plants goes through sine waves, now in very long supply and then in very short supply. The latest I heard was that it's in short supply in Europe. And so the situation has changed, rather quickly. Availability of cheap naphtha from Europe will limit the construction of additional plants.

Richardson: I don't think that there are any special catalytic problems, this process that doesn't exist in general. But the problems here do point out the need for expanded research in these areas.

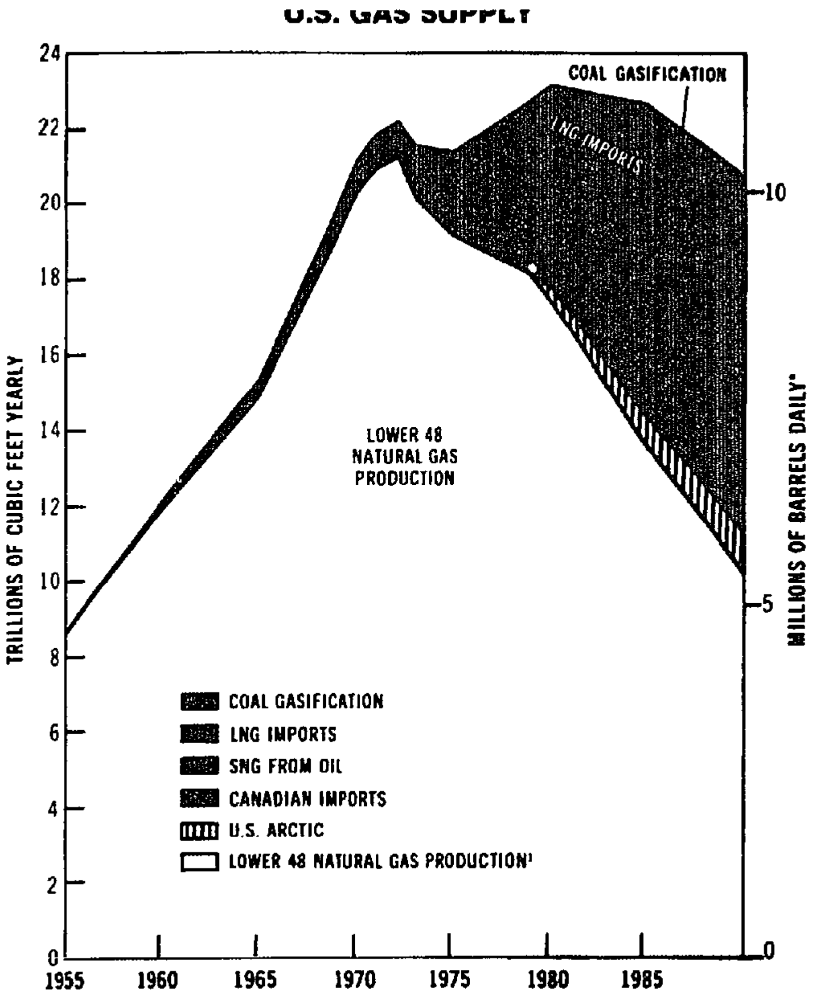
Heinemann: One catalytic problem is in the use of potassium as a promoter. Potassium is quite volatile and goes away and the catalyst deactivates very rapidly because of the loss of potassium. Sodium, on the other hand stays better but is not anywhere near as good a promoter as potassium is. So here is a real good problem of how to promote the carbon steam reaction with something that is stable at these temperatures for long periods of time.

U.S. ENERGY SUPPLY THE ROLE OF NATURAL GAS



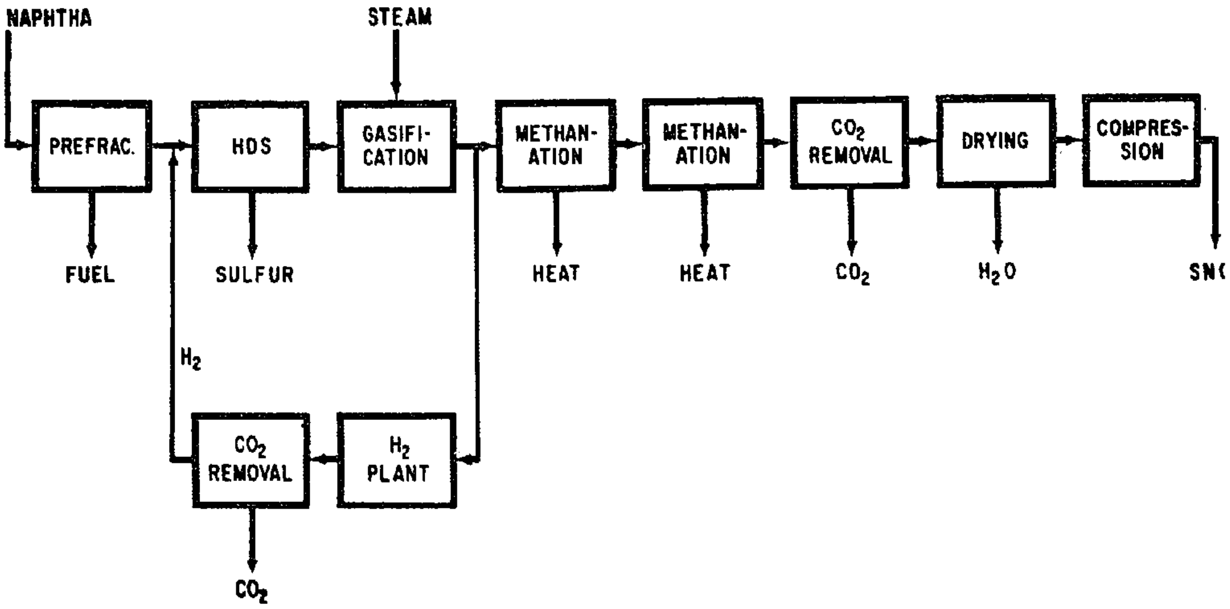
*Crude Oil Equivalent

1a

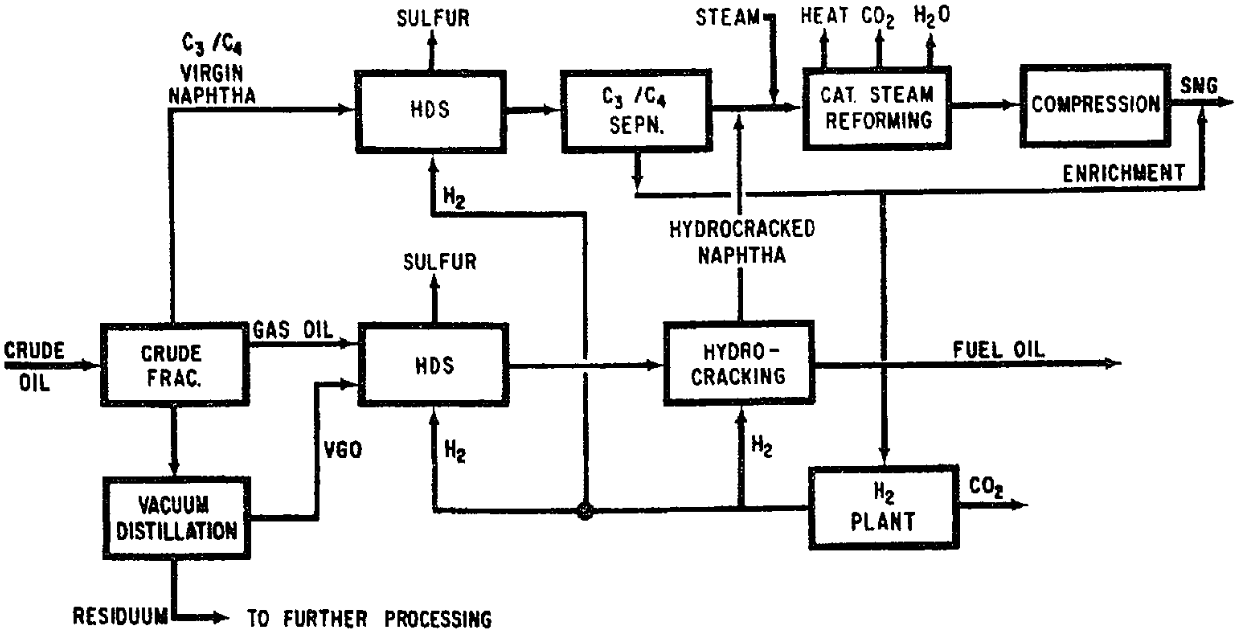


FEEDSTOCK	PROCESS	COMMERCIALLY PROVEN	ADVANTAGES	LIMITATIONS
LPG, NGL, 400°F NAPHTHA	LTCSR	YES	BUILT QUICKLY MODEST CAPITAL	IMPORT PERMITS DOMESTIC SUPPLY CARBON DEPOSITION
CRUDE OIL	HC/CSR	YES	FLEXIBLE SUPPLY	CARBON DEPOSITION
650°F DISTILLATES	GRH	NO	FLEXIBLE SUPPLY	HIGH CAPITAL AROMATICS SYNTHESIS
CRUDE OIL	FBH	NO	FLEXIBLE SUPPLY	HIGH CAPITAL AROMATICS SYNTHESIS
CRUDE OIL, RESIDUALS	PO	YES	FLEXIBLE SUPPLY	LOW THERMAL EFFICIENCY RELATIVELY EXPENSIVE

PROCESS ROUTES	PROCESS	DEVELOPER	FEEDSTOCK HYDROCARBON
STEAM REFORMING			
LOW TEMPERATURE CATALYTIC	CATALYTIC RICH GAS	BRITISH GAS	LIQUEFIED PETROLEUM GAS NATURAL GAS LIQ. 400°F NAPHTHA
	GASYNTHAN	BASF/LURGI	
	METHANE RICH GAS	JAPAN GASOLINE	
	MANAGAS	HALDOR-TOPSOE	
HIGH TEMPERATURE CATALYTIC	—	VARIOUS COMPANIES	430°F NAPHTHA
HYDROGENATION			
THERMAL	GAS RECYCLE HYDROGENATION	BRITISH GAS	650°F DISTILLATES
	FLUID BED HYDROGENATION	BRITISH GAS/ OSAKA GAS	DISTILLATES & CRUDE OIL
CATALYTIC	HYDROCRACKING	VARIOUS COMPANIES	VAC. DISTILL., DEASPH. RESID.
OXIDATION			
THERMAL	PARTIAL OXIDATION	VARIOUS COMPANIES	CRUDE OIL RESIDUUM, ASPH.


NAPHTHA
STEAM
PREFRAC.
HDS
GASIFI-CATION
METHAN-ATION
METHAN-ATION
CO_2 REMOVAL
DRYING
COMPRES-SION
FUEL
SULFUR
HEAT
HEAT
CO_2
H_2O
SN
H_2
CO_2 REMOVAL
H_2 PLANT
CO_2

4


SULFUR
STEAM
HEAT
CO_2
H_2O
C_3/C_4 VIRGIN NAPHTHA
HDS
C_3/C_4 SEPN.
CAT. STEAM REFORMING
COMPRESSION
SNG
H_2
ENRICHMENT
HYDROCRACKED NAPHTHA
SULFUR
CRUDE OIL
CRUDE FRAC.
GAS OIL
HDS
HYDRO-CRACKING
FUEL OIL
VGO
H_2
H_2
VACUUM DISTILLATION
H_2 PLANT
CO_2
RESIDUUM
TO FURTHER PROCESSING

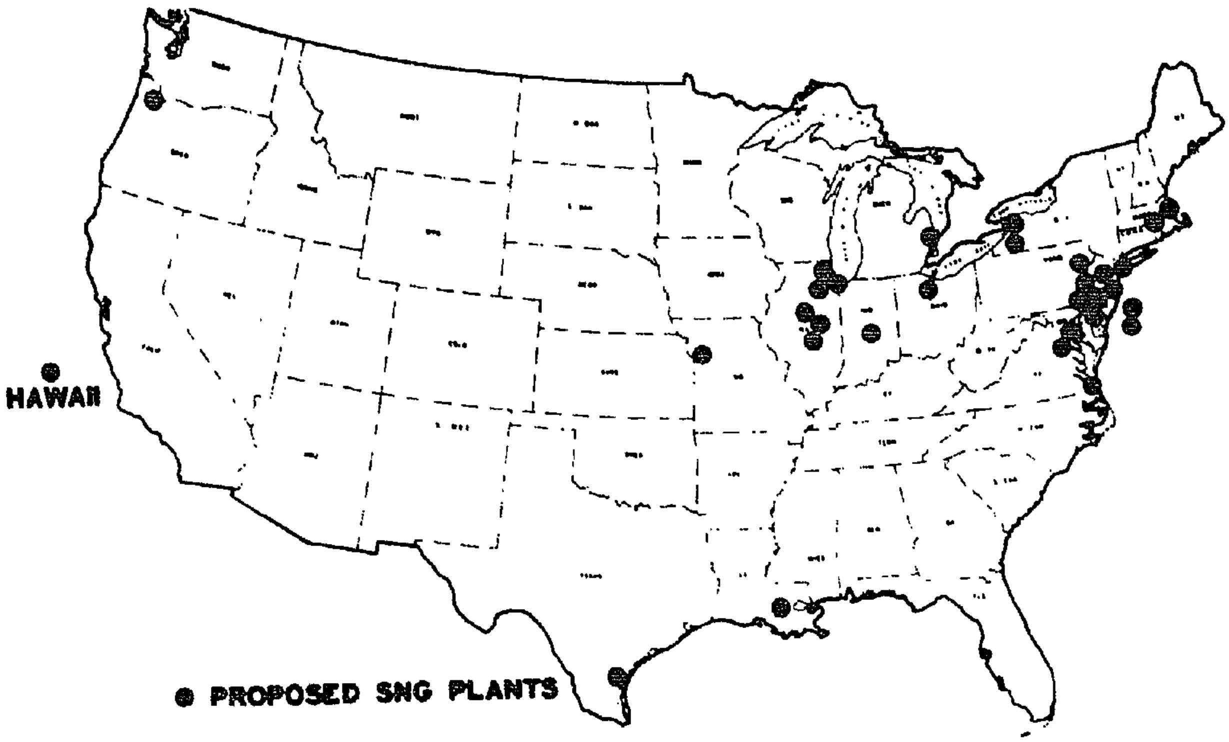
5

STATUS	NO. OF PROJECTS	FEEDSTOCK TYPE	FEEDSTOCK RATE MBPSD	SNG CAPACITY MMSCFD	CAPITAL COST $ MM
CONSTRUCTION	7	NAPHTHA	37	170	75
		LIGHT ✳	188	686	204
			225	856	279
ENGINEERING OR PLANNING	24	NAPHTHA	717	3308	922
		LIGHT ✳	96	430	135
			813	3738	1057
TOTALS	31	NAPHTHA	754	3478	997
		LIGHT ✳	284	1116	339
			1038	4594	1336

✳ INCLUDES:
PROPANE, NATURAL GAS LIQUIDS & LIQUEFIED PETROLEUM GASES

LOCATION	NUMBER OF PROJECTS	CRUDE OIL RATE MBPSD	SNG CAPACITY MMSCFD	FUEL OIL CAPACITY MBPSD	CAPITAL COST $ MM
EAST COAST	3	430	530	270	550
GREAT LAKES	1	100	100	50	70
GULF COAST	4	425 ✳	1600 ✳	✳	1140
	8	955 ✳	2230 ✳	320 ✳	1760

✳ INCOMPLETE INFORMATION



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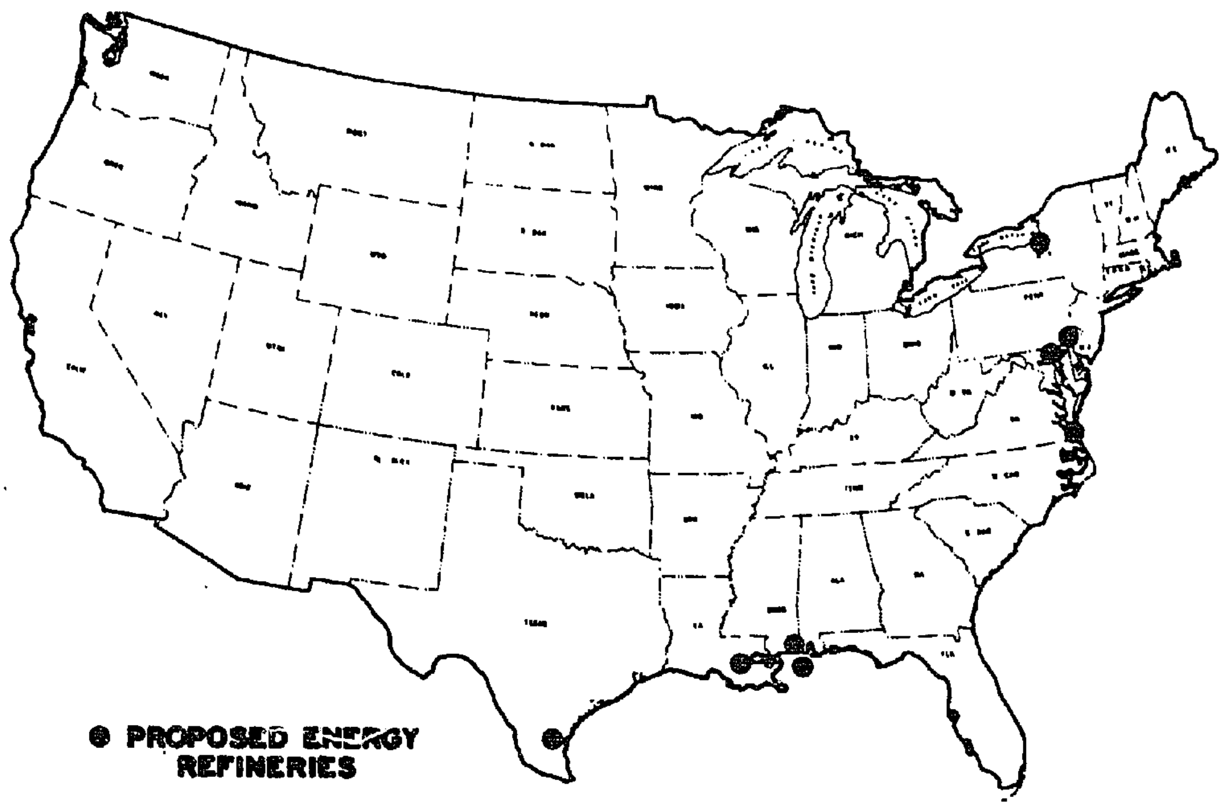


9

NOT REPRODUCIBLE

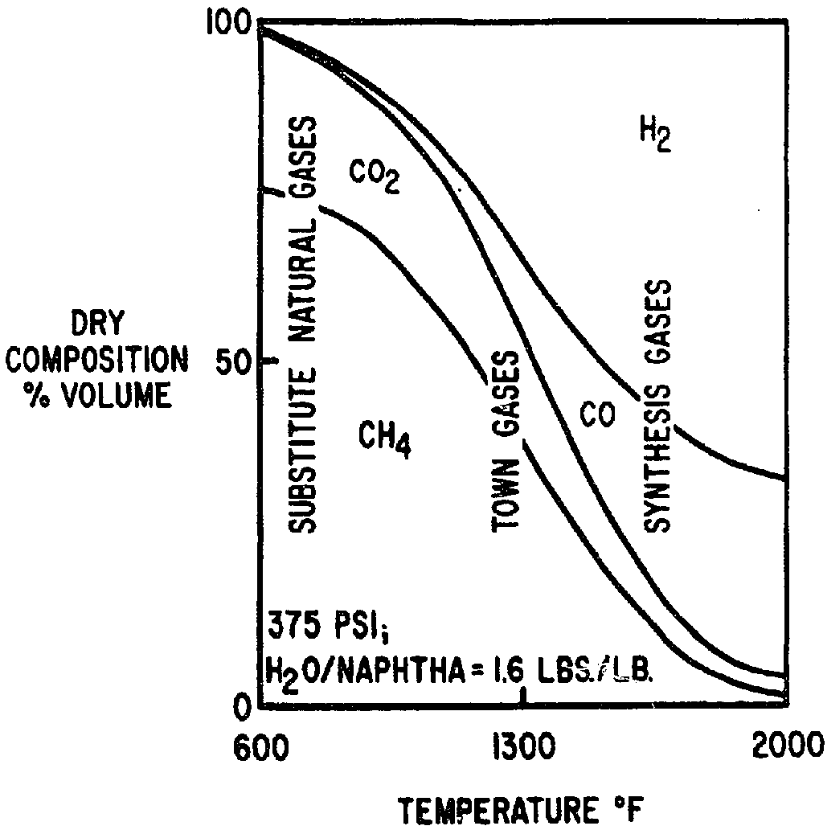
CHEMICAL REACTIONS

(1) $C_nH_m + nH_2O \rightarrow nCO + (n+\frac{m}{2})H_2$

(2) $C_nH_m + (2n - \frac{m}{2})H_2 \rightarrow nCH_4$

(3) $CO + H_2O \rightleftarrows CO_2 + H_2$

(4) $CO + 3H_2 \rightleftarrows CH_4 + H_2O$



SNG CATALYST REQUIREMENTS

Activity:

- Active component
- Large surface area
- High effectiveness factor

Life:

- Low sintering rate
- Low accumulation of "coke"
- Resistant to sulfur

IMPROVEMENTS

Reduced coking

Less sintering

Higher activity

COMMERCIAL CATALYSTS

Ni: 30 - 75 wt %
(30 - 50 M^2/g)

Supports: Silicate, silica, alumina
Preparation: all methods
Promoters: K(Ba); Mg; $CuCr_2O_4$
?
Other: graphite, etc.

SNG PROCESS NEEDS

High activity for wide range of naphtha compositions

Long life under full load, continuous operation

CATALYTIC REMOVAL OF SULFUR, NITROGEN, AND HEAVY METALS DURING COAL GASIFICATION

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First of all a lot of people think there is basic research and applied research but there is another kind which I would characterize as exploratory research, exploratory research which often is not done in the university. It is very necessary to try things out, which certainly industrial laboratories do; in fact, the industrial and government laboratories, including Bureau of Mines and Coal Research are doing profitable exploratory research. People in industry don't particularly get involved with committees in which they throw out their best ideas to these committees and suggest innovative research. So first I protest the makeup of the committee (Hightower panel), being composed solely of academic people, as not being in the best interests of representing a complete viewpoint of this meeting (my personal comment).

Second, I thank you Bill Bailey for the invitation to say something about liquefaction of coal at the Bureau of Mines. I mention three activities: one is the use of carbon monoxide in steam to make nascent hydrogen or activation via a formation which is on its own an interesting chemical reaction. The second is reductive alkylation which shows you don't have to hydrogenate coal in order to make it soluble but if you add methyl groups you can do this. The third is the turbulent catalytic reactor which is a fixed bed of catalysts and ties in with desulfurization processes that we heard Harold Beuther talk about. I second strongly his comments on the desirability for understanding desulfurization of petroleum residual, which is also important to coal catalysis where the same problems exist, and also shale catalysis.

Until now we have been talking of historical research; we are now entering an era of future research, to do with coal and oil shale. Petroleum catalysis has had a good history with tremendous impetus which certainly will continue; we need to pull oil shale and coal processing technology out of the 1930's and into the 1970's.

Liquefaction and gasification of coal and the removal of impurities from stack gas are three technologies of extreme importance because of the coal resources which we have. A back of the envelope calculation shows that we have more coal than the Arabs have oil. So in the year 2030, come around, and see the Arabs import coal from this country. Anything that can be done with coal gasification will release other more scarce fuels for use in other applications. As Jim Richardson mentioned, gas now supplies 33% of our energy. Its use has been growing at about 6% a year, more than gasoline, more than petroleum; and it is significant that the price of new gas supplies has increased seven fold. New gas instead of being about 20¢ a thousand cu. ft. is going to be about $1.40 per thousand cu. ft.

Gasification of coal can be carried out to make gas of 150 BTU per cubic foot, low compared with methane at 1000 BTU cubic foot. It is of growing interest for utilization in power plants particularly with combined power cycles; one makes it with air instead of oxygen, then follows with hot gas cleanup.

High BTU gas is methane having 1000 BTU per cubic foot. In the hydro-gasification processes practiced by the Hi-Gas process of Institute of Gas Technology, one makes hydrogen first and then hydrogenates coal. Most of the other processes have a steam-oxygen reaction with coal to make a mixture of hydrogen, CO, CO_2, and methane. While this isn't the subject of this meeting, the engineering of coal processing is way behind, techniques of fluid bed processing, feeding devices, and the problems of handling of solids.

We've heard already something about the Lurgi process, a so-called fixed-bed process. A second alternative is fluid bed processing under pressure and a third alternative is an entrained bed. The entrained bed is of interest because it operates at high temperature, in the range for making hydrogen and so it is of interest for hydrogen production.

Slide 1 indicates the distribution of coal in the United States and it ought to be of interest for reasons of national security that coal is widely located. Anthracite is mostly exhausted. Bituminous coal, sub-bituminous and lignites are widely distributed. The second slide shows chemical composition of coal including hydrogen/carbon ratios; note that lignite contains 21% oxygen; even the high volatile A has 7% oxygen, and of course nitrogen and sulfur are relatively high. Next slide, 3, is a summary of certain pilot plants which are being built; in Chicago, a Hi-Gas pilot plant, in Rapid City, South Dakota, a so-called "CO_2 acceptor process", the Bureau of Mines Synthane process, and a pilot plant is being constructed using the Bi-Gas process. There are four large pilot plants. Each pilot plant processes about a carload of coal a day, and makes about a million and a half cubic feet of methane per day. These are all fluid bed processes, in contrast to the fixed bed Lurgi process which is in operation in various parts of the world but not in the United States. Our game plan is to design and operate these pilot plants for decision-on-construction about 1976 and construction of a demonstration plant by 1979. Three groups say that they plan to build a plant now, namely El Paso, Texas-Eastern and Madison-Wisconsin. To proceed now you must combine a Lurgi process and a methanation process built along the lines that Jim Richardson was talking about.

The next slide, 4, shows a flow diagram of the Sythane process, in which powdered coal is mixed in fluid form with steam and oxygen at 1800 degrees Fahrenheit and 1000 lbs. pressure to produce a mixture of CO-hydrogen-CO_2-methane at 1800 degrees. At this pressure about half the total possible yield of methane is produced; at higher temperatures more conversion of the methane occurs into CO and hydrogen. After some purification there is a shift reaction in which the CO and steam are reacted to form hydrogen and CO_2 to provide the hydrogen to CO ratio at three to one mole ratio; next a scrubber to remove the H_2S and CO_2, followed by final purification and then a methanation step in which the CO and hydrogen are combined to form methane, making a product having something like 95% methane and 5% hydrogen.

There are several chemical reactions here which can be influenced by catalysts. The shift is carried over a catalyst and of course the methanation is carried over a catalyst. If the first reaction of slide 5, the steam-carbon reaction would occur at low temperature to produce CH_4 and CO_2 you'd be in great shape because you have both a molecular balance and a thermal balance. But the steam-carbon reaction goes rapidly only at high temperature and methanation at low temperature. Bugs can react with carbohydrates at room temperature to produce a mixture of CO_2 and methane, but we have to go to 1800 degrees Fahrenheit since the carbon-steam reaction of gasification is slow. One wishes to have a gasification catalyst which is active at lower temperature, slide 6, and then you'll have more methane than the equilibrium mixture. Some of the catalysts active in the steam-carbon reaction are potassium oxide and sodium oxide.

Next slide, 7, shows some catalysts which have been used and you see the potassium carbonate speeds up the gasification by 62% and makes 91% more CO and 83% hydrogen while not so much methane but it does speed up gasification. Better catalysis of this reaction could be very important in cutting down on the capital cost.

The next slide, 8, shows something about the shift reaction and types of catalysts used.

The next slide, 9, focuses on the reactions in methanation; there is a problem in preventing formation of carbon on the catalysts. CO_2 is not much hydrogenerated in the presence of CO.

Next slide, 10, shows something about the mechanism. Fred Steffgen and I have a fairly elaborate review of methanation about to be issued in the next issue of Journal of Catalysis (actually, Catalytic Reviews). One theory which is similar to the Fischer-Tropsch postulates forming a complex containing oxygen and adding hydrogen as shown, and finally forming methane. Of course methanol can be formed by a different set of catalytic reactions. One of the places where work is needed is on the mechanism of methanation. The Fischer Tropsch reaction interestingly enough has been investigated more than methanation. Investigators have used infrared measurements, kinetics and chemisorption studies. So there are classical tools to use to try to decide what are the nature of these intermediates and how they depend on catalysts and the influence on their selectivity.

The next slide, 11, shows four catalysts with platinum and palladium, their corresponding products, including methane, ethane, butane and propane; for ruthenium there are liquids formed as well as lighter products. In the past we have used nickel catalysts and sometimes ruthenium to make methane, but in the future we will want to broaden the product so that both methane and other products result. For example, for pipeline gas for transportation, one may want not only methane, but also higher-density materials such as ethane, propane, and so on. Such products are needed both for chemical use and also for transport economics. To recapitulate, by changing the catalysts or catalyst condition the products of hydrogenation of CO can make not only methane, but a variety of products.

The last slide, 12, shows the so-called tube-wall reaction. I put it in because people at the Bureau of Mines made an interesting type of invention in which they flame-spray an alloy of nickel and aluminum on a tube. They then leach this and make a Raney nickel in place, with metallic contact with the tube, and then by running Dowtherm on the inside, and having the catalyzed reaction on the outside of the tube, have a very high heat transfer. This is just one example.

The Bureau of Mines has tackled underground gasification of coal by a way that has in the past been given up several times, but has new opportunities, including catalytic opportunities.

There are two other fuels which come from coal gasification. One is hydrogen, this is a major opportunity, both for hydrogasification and hydroliquefaction, and of course for hydrogen fuels in their own use. The other is to form methanol from the products of gasification. This is not exactly a Fischer-Tropsch, instead it is one type of hydro-liquefaction. This is an opportunity to form a mixture of CO and hydrogen, combine these to form methanol which is a liquid fuel. You can do many things with methanol, for example, as an auto fuel it has 130 octane.

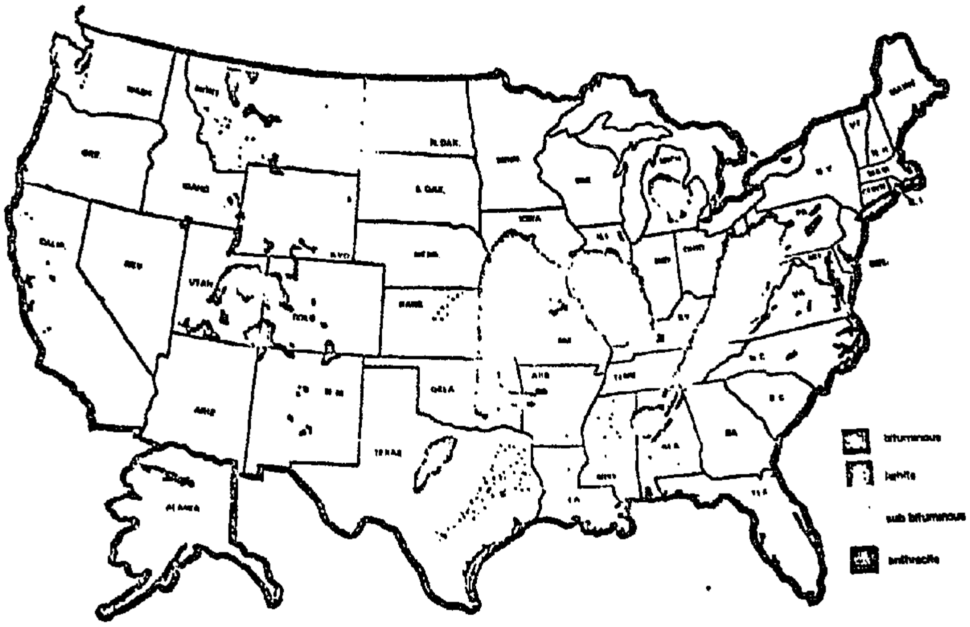
Well, the burden of my talk is there are a number of catalyst opportunities, in each of the steps in the gasification, of the shift, and of the reaction of carbon monoxide and hydrogen. By catalytic improvements there is the opportunity to reduce the capital cost significantly, and to make a more useful distribution of products. The directions are clear, we want to increase catalytic activity, and lower sensitivity to catalyst poisons. We want to lower the temperature and reduce the cost and produce more methane. Thank you.

Discussion

Heineman: It is a very interesting and informative articles that Alex and Stefkin have written on "Methanation," which will appear in the Catalysis Reviews not in the Journal of Catalysis.

Hightower: Is this underground gasification, are catalysts being used?

Mills: The natural salts in lignites such as sodium salts are catalysts and so are iron compounds. These are natural catalysts which are being used.



1

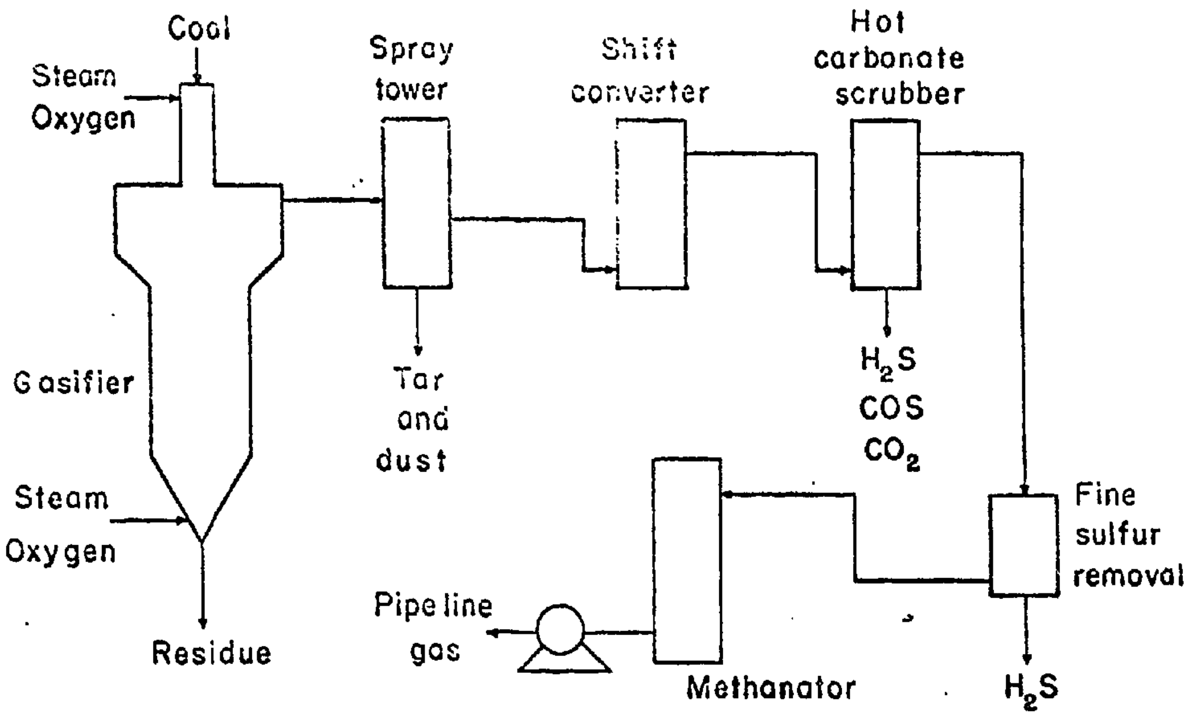
Chemical Composition of Some Coals and Petroleum

	Anthracite	High Volatile A. Bit.	Lignite	Petroleum Crude	Gasoline	Toluene
C	93.7	84.5	72.7	83-87	86	91.3
H	2.4	5.6	4.2	11-14	14	8.7
O	2.4	7.0	21.3			
N	0.9	1.6	1.2	0.2		
S	0.6	1.3	0.6	1		
H/C atom ratio	0.31	0.79	0.69	1.76	1.94	1.14

2

Coal Gasification Pilot Plants

Hygas	(Chicago)
CO_2 Accystor	(Rapid City)
Bi Gas	(Homer City)
Synthane	(Bruceton)



. Synthane Coal Gasification Process.

$C + 2H_2O \longrightarrow CO_2 + CH_4$

$C + H_2O \longrightarrow CO + H_2$ Gasification

$CO + H_2O \longrightarrow CO_2 + H_2$ Shift

$CO + 3H_2 \longrightarrow CH_4 + H_2O$ Methanation

$C + H_2O \rightarrow CO + H_2$ GASIFICATION

Need - Catalyst Active at Low Temperature

- High Steam Utilization

- Inexpensive, Recycle

Mechanism - High Catalyst Mobility

$CO + H_2O \rightarrow CO_2 + H_2$ SHIFT

Iron - Chromium Oxide

Copper - Zinc

MoO_3 - Al_2O_3

Need - Low Temperature Activity

- Low Sensitivity to Poisons

Mechanism - Formate Ion

(1) $3H_2 + CO \longrightarrow CH_4 + H_2O$

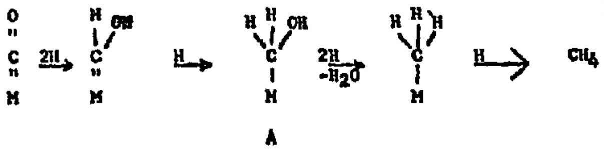
(2) $2H_2 + 2CO \longrightarrow CH_4 + CO_2$

(3) $4H_2 + CO_2 \longrightarrow CH_4 + 2H_2O$

(4) $CO + H_2O \longrightarrow CO_2 + H_2$

(5) $2CO \longrightarrow C + CO_2$

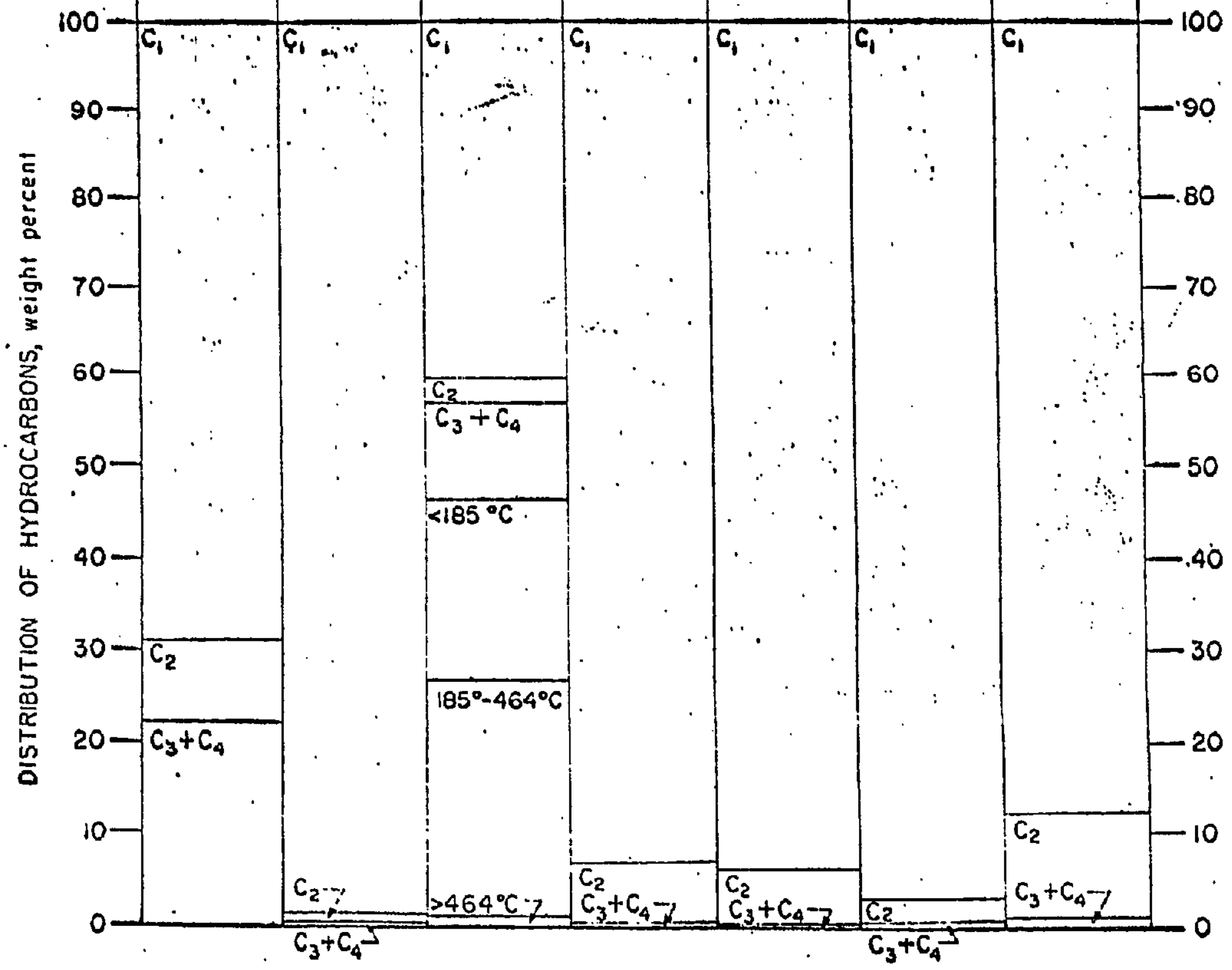
(6) $2H_2 + C \longrightarrow CH_4$



CH_4	H_2	CO	C gasified
Li_2CO_3 - 21	K_2CO_3 - 83	K_2CO_3 - 91	K_2CO_3 - 62
Pb_3O_4 - 20	Li_2CO_3 - 55	Li_2CO_3 - 72	Li_2CO_3 - 40
Fe_3O_4 - 18	Pb_3O_4 - 39	Fe_3O_4 - 60	Pb_3O_4 - 30
MgO - 17	CuO - 37	Cr_2O_3 - 55	Cr_2O_3 - 26
Cr_2O_3 - 16	MgO - 35	Pb_3O_4 - 52	MgO - 26
CuO - 15	Fe_3O_4 - 33	CuO - 49	Fe_3O_4 - 23
Al_2O_3 - 14	Al_2O_3 - 33	Al_2O_3 - 45	CuO - 22
K_2CO_3 - 6	Cr_2O_3 - 25	MgO - 28	Al_2O_3 - 22

Coal Gasification - Percentage Increase of CH_4, H_2, CO and Carbon Gasified Upon Addition of 5% of Salts Shown.

Catalyst	Pt	Pd	Ru	Rh	Os	Re	Mo
Cat No	L1138	L1140	L1141	L1139	L1163	L1154	L6137
Run No	Z360	Z362	Z363	Z361	Z408	Z394	Z353
Temp °C	513	499	222	441	600	451	420
SVH	297	318	303	302	295	281	288
CO_2 – free contraction, %	38.2	24.8	67.1	64.8	57.5	64.4	44.2
Conversion %	56.4	35.5	79.7	86.7	70.0	85.5	56.4
Usage ratio H_2/CO	1.8	2.2	2.4	2.4	2.3	2.4	1.8



Comparison of operating conditions and selectivity using $3H_2 + 1CO$.

ENVIRONMENTAL RESTRICTIONS AND THEIR RELATIONSHP TO DOD CATALYSIS NEEDS

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Environmental concern has only in recent years reached levels such that it could influence the needs in catalysis, even if indirectly. In the context of this conference, environmental concerns can be grouped under two headings. The first heading would include those which grow out of the operations of oil refineries which also are catalytic in nature, and lead to pollutant emissions. The second would include those growing out of other operations, such as the use of motor vehicles, for which catalysts might provide a means of emission control. Because other presentations to be made at this conference will address the latter of these two headings directly, it will not be of primary concern here. Discussion in this paper will center on the problems of pollutant emissions derived from refinery operation, and how concern for these emissions may influence catalysis needs.

Refinery pollutant emissions can be classified first according to their physical state: solid wastes, liquid wastes and air pollutants. A certain amount of the residual material left after chemical processing and attempts at cleanup inevitably will wind up as solid waste. Such materials in present quantities usually can be handled without difficulty within sanitary landfills, and so are no problem and will not be discussed further here.

Liquid waste effluents usually emerge in a stream of wastewater. These can be handled at acceptable cost by conventional treatment methods, and only a very brief discussion will be presented.

Air pollutant emissions comprise the principal refinery problem for which, though a substantial measure of control exists, there is a significant opportunity for further improvement. The kinds of air pollutants of concern include particulates, both in solid and in liquid form; gaseous sulfur compounds such as sulfur dioxide; carbon monoxide; hydrocarbon gases; and gaseous nitrogen oxides. Sulfur compounds pose a uniquely important problem, both because of their pervasive presence in fossil fuel source materials, and the important problems for both people and other living matter which may be a consequence of their release to the biosphere. But because the problems of sulfur removal will be discussed extensively elsewhere at this conference, no further discussion will be included in this paper.

Carbon monoxide and hydrocarbons represent valuable resources within a refinery and as such are fully utilized. Current state of the art is such that emissions of these materials have been or can readily be reduced to a level of no pollutant significance. This leaves two sources of atmospheric emissions to be considered in this presentation: nitrogen oxides and particulates. It will be shown that there are current problems related to each of these sources which are of interest and of considerable potential importance. While the relationship is indirect, these problems are dependent on current and future uses of catalysis, both within and external to petroleum refineries.

Liquid Refinery Wastes

The liquid wastes which are a result of refinery processing of crude oils are discarded as a part of the wastewater stream. Without control, these can destroy the ecology of either the fresh or saltwater receiving body. Fortunately, water pollution problems have long been recognized. Effective, relatively low cost treatment methods for purification have been developed. Proposals for effluent limitations are now before the Environmental Protection Agency in the form of a contractor's report (Roy F. Weston, Inc.)[1]. The proposals are at two levels: the "best practicable control technology" today, recommended for implementation by 1977, and "best available controls," which would be recommended for implementation by 1983.

The "best practicable" technology relies on two methods for control: (a) in-process controls such as the segregation of contact and non-contact water streams, and the use of strippers to remove hydrogen sulfide from sour water streams; and (b) a one-stage activated sludge treatment followed by granular media filtration. For a typical refinery complex which performs the full range of topping, cracking, production of intermediates, petrochemicals and lube oils, suggested effluent limitations are as shown in Table 1A. The eight pollutants are (5-day) biological oxygen demand, chemical oxygen demand, total organic carbon, suspended solids, oil and grease (carbon tetrachloride extractables), phenol, ammonia nitrogen and sulfides.

The "best available" control technology suggests first a reduction in effluent volume through the recycle of substantial portions of the wastewater flows, reducing the volume of effluent on which limitations are calculated. In addition, activated charcoal adsorption is added to the wastewater treatment process. The proposed limitations are listed in Table 1B for the same refinery description used for Table 1A.

There are costs to be included, of course, in achieving either of these standards. One cost assuming rapidly increasing importance these days is the cost of energy. Fortunately, the energy required to add these effluent treatment steps to a refinery is negligible. The dollar cost for an approximately 100,000 barrel per day plant is estimated at $2.2 million per year. Converted to an added cost per gallon of product, this represents about 0.15 cents per gallon, much too small to influence any retail market.

Thus though we see that liquid waste problems for refineries do exist, and though we recognize that in some instances refinery effluents may have caused severe water pollution, there is a technology available at a reasonable cost which is sufficient to solve essentially all problems.

Table 1A

"Best Practicable" Effluent Limitations

(pounds/1000 bbl per stream day)

BOD_5	COD	TOC	SS
4.6	42.5	8.2	3.1
O&G	**Phenol**	**Ammonia**	**Sulfide**
1.5	0.031	1.8	0.03

Table 1B

"Best Available" Effluent Limitations

BOD_5	COD	TOC	SS
1.28	8.9	3.8	1.28
O&G	**Phenol**	**Ammonia**	**Sulfide**
0.25	0.0005	0.60	0.026

Atmospheric Refinery Emissions - Nitrogen Oxides

Nitrogen oxides are formed as a byproduct of all fossil fuel combustion. As a consequence, large petroleum refineries constitute major point sources of these pollutants. Nitrogen oxides are particularly important as a constituent of photochemical smog, working in sometimes confusing and apparently contradictory ways.

As just one example, nitrogen dioxide as the light-absorbing medium is essential to the initiation of the photochemical process by which oxidant is formed. At the same time, nitric oxide, the primary combustion byproduct, acts as a scavenger to remove oxidant. This is a particularly important effect in the neighborhood of strong sources such as freeways, power plants and refineries. Of course, the scavenging step produces more nitrogen dioxide which in turn leads to the eventual amplified production of oxidant. But the ultimate oxidant production occurs at a much later time and a different location than the infusion of source nitrogen oxides and the hydrocarbons also essential to the process. Useful approximate computer models have been developed. However, the length and complexity of the reaction chain and meteorological events understood to lie between sources and receptors of photochemical oxidant make exact analysis impossible.

From the standpoint of air quality management, the majority of informed thinking at present appears to be that the problem is most effectively solved by very tough restrictions on hydrocarbon emissions. Because nitric oxide acts to terminate the photochemical chain through formation of peroxyacyl nitrates, this school of thoughtbelieves that at most a moderate level of nitrogen oxide control may be necessary or desirable.

However, a strong alternative viewpoint has been developing among some of those most competent in atmospheric photochemistry. By this view, the tough hydrocarbon controls are believed to be necessary. But it is also believed that substantially greater control of nitrogen oxides will also prove necessary before the major reductions in oxidant needed to portect health are achieved. (It is important to note that imperfections in past atmospheric monitoring methods in no way enter these considerations.)

While it is uncertain now as to which of these viewpoints will prevail, it is certain that within key urban centers plagued with photochemical smog nitrogen oxide emissions must be reduced. Reduction from automotive sources is proving extremely difficult and costly, including a large energy cost. Thus any reduction from stationary sources, including refineries, conceivably could prove a much more cost effective approach to the problem.

Nitric oxide formation accompanying fossil fuel combustion occurs by a Zeldovich chain:

$$N_2 + O \longrightarrow NO + N$$

$$N + O_2 \longrightarrow NO + O$$

A method for control in automotive fuel combustion, exhaust gas recirculation, was developed and reported on in the literature as early as 1958. Extension of the basic ideas behind this approach to stationary processes, though obvious, required about ten years. The nitric oxide formation reaction is very fast, and so approaches equilibrium favoring nitric oxide formation at the high temperatures characteristic of combustion. Thus control requires, first, reducing peak combustion temperatures and, second, reducing the time of exposure to high temperatures.

Stationary source control schemes have evolved along several lines[2]. One approach is to control the mixing of fuel and air, delaying the combustion process long enough for radiative cooling to occur and also so that entrainment of the combustion products into the air and fuel can take place. Two stage combustion also is utilized. In this process some burners are operated fuel rich, and additional air is provided through a staggered pattern of burner ports used to provide air only. Reduction of the preheat given combustion materials also can be utilized, as can premixing of burner air and recirculating exhaust gases.

The delayed mixing and two-stage combustion have proved to be successful retrofit approaches for existing units. When employed in atomized-oil-fired units, however, the bulk of the combustion chamber no longer exhibits recognizable burner plumes. Instead, the chamber appears to be filled with a ball of fire. Large amounts of soot are formed, which differs from the conditions for natural-gas-fired units, even with two-stage combustion. Dr. Donald K. Edwards and his group at UCLA have undertaken a systematic study of the combined radiative transfer and simultaneous turbulent convection accompanying this process[3]. It is his belief that radiative heat transfer in boilers and furnaces can be significantly improved, lowering combustion temperatures with significantly less production of nitric oxide.

The flame front model geometry is sketched in Figure 1. Two plane, parallel black isothermal cooled walls contain a turbulent gas. The gas contains soot which can both absorb and radiate heat. In heterogeneous combustion, volatiles may burn in a thin reaction zone between fuel-rich and oxygen-rich gases, while other fuel particles or eddies of air sustain combustion throughout the chamber. The thin reaction zone is modeled as a plane heat source, and the volume combustion by a volume heat release. In addition to radiation, there is a volume heat release due to convection.

To evaluate the effect of temperature changes on nitric oxide formation, use was made of already established Zeldovich-based reaction kinetics. Reaction

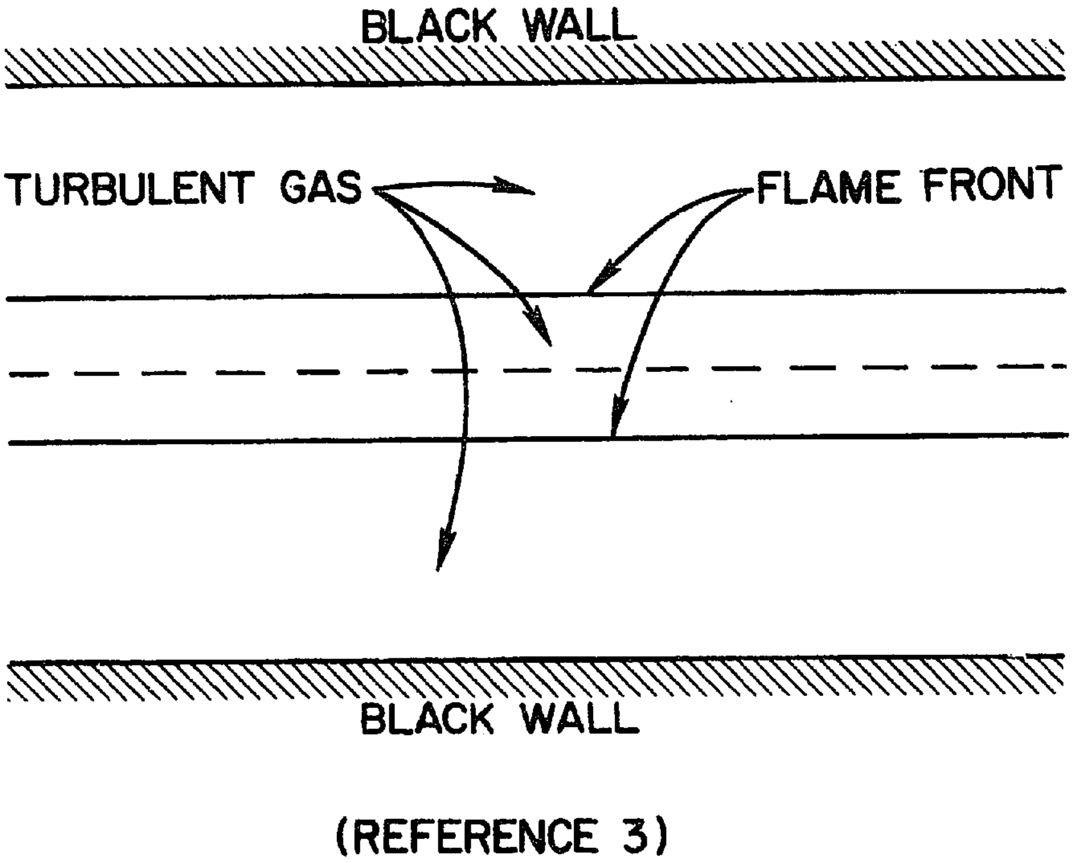

Figure 1. Flame Front Model Geometry.

was achieved in two steps. First the frozen concentration that would result from a short exposure (0.05 second) at the flame front was found. Then the concentration resulting from a longer time (1 second) at the volume average temperature was obtained. An upper limit to the nitric oxide concentration is the sum of these values.

The results obtained are shown in Figure 2 and are indeed remarkable. The quantity of nitric oxide formed, either through flame front heat release or volume heat release is seen to be strongly dependent on the amount of soot present and thus the extent of radiative transfer. There is a sharp minimum near an optical depth of 2, indicating that a moderate amount of soot is highly beneficial in promoting high heat transfer rates in the radiant section of the boiler.

The reasons for this behavior are not hard to recognize. In a turbulent gas there is a microscale recirculation brought about by turbulent eddies of exhaust gases mixing with combustion air. On a chance basis, some of these eddies will have been cooled by the strong radiative cooling mechanism which soot can provide. At the same time, the visibility of the cold wall must not be masked by too much soot.

Practical implementation of these results also can be achieved. Control of soot formation during mixing-controlled or two-stage combustion can be achieved through exhaust gas recirculation or steam injection. Optical depth can be controlled through design which introduces the appropriate radiant wall surface. The practical goal which can be set would be to reduce nitric oxide emissions to no more than one fourth of presently projected values; that is, to levels below 55 ppm for liquid fuels. For an area such as the Los Angeles metropolitan

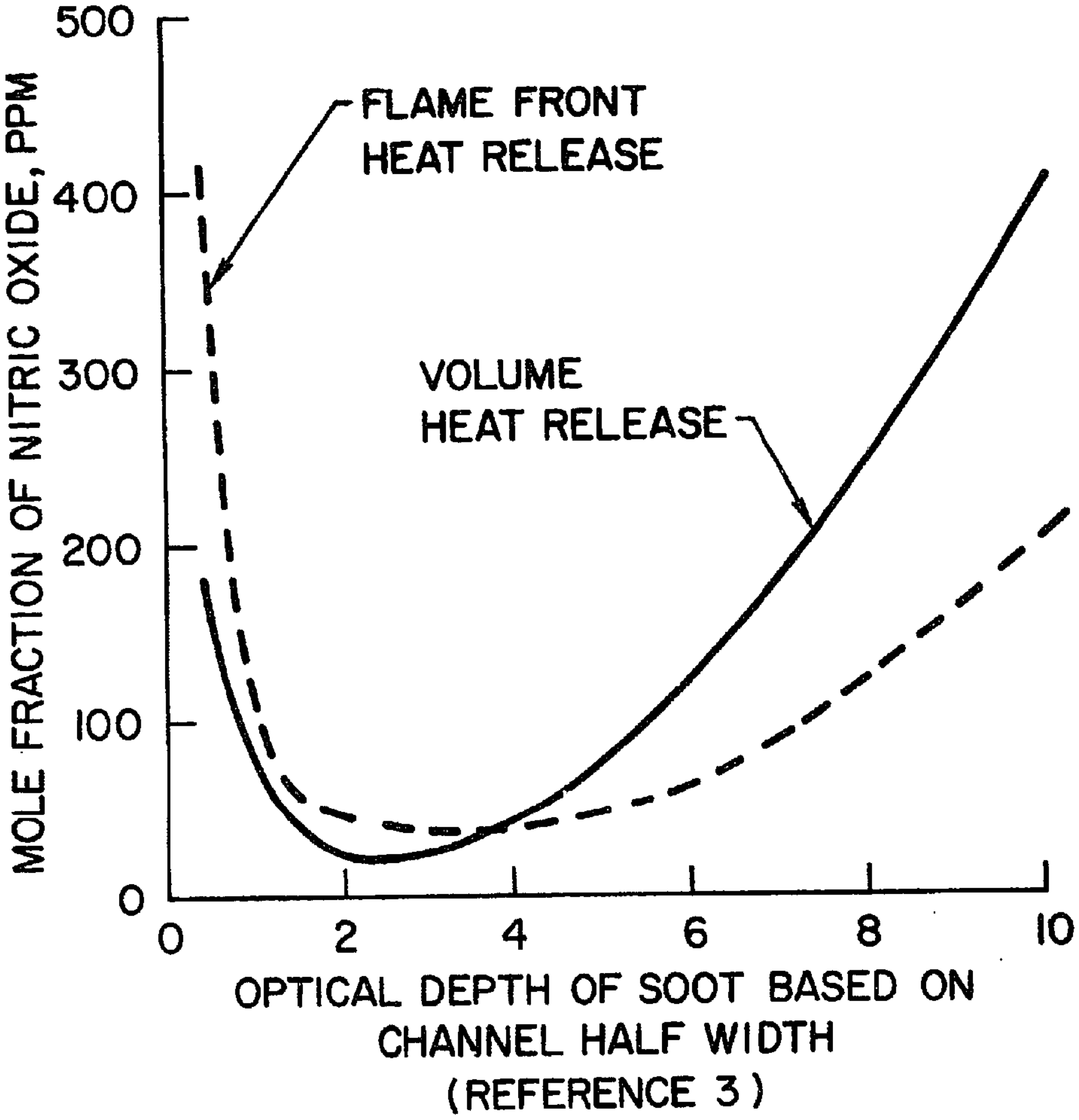

Figure 2. Nitric Oxide Emissions vs Optical Depth of Soot.

air quality control region this could provide very significant relief.

However, there still remains a need to show just how reduction in nitrogen oxide emissions relates to catalysis needs. If stationary contributions are reduced enough, a less severe reduction in automotive sources may prove tolerable. This can influence catalysis needs in several ways. First, chemically reducing catalysts in automotive systems may never prove to be necessary; simpler control schemes may suffice. Furthermore, less stringent specifications for automotive fuels may be tolerated. This would strongly influence refinery operation and catalysis back at this source. In point of fact, we cannot at this time define sharply the indirect effects of the nitrogen oxides controls suggested. But we can say with certainty that there is a strong indirect relationship, and that the overall effect would be to ease catalysis needs.

Atmospheric Emissions - Particulates

Suspended particulates in ambient air consist of both liquid droplets and solid particles from a wide array of sources. Liquid droplets which in part contain end products of the atmospheric photochemical chain of reactions have been a matter of considerable concern, and so their formation has been studied to a reasonable extent. Dust-like particles also are present. Except for concern as to the physical aggregation and disaggregation processes which determine sizes of particles observed, and recent concern for heavy metals content, etc., these appear to have received much less sytematic study. Typical particles sizes are such that more than half lie in the respirable range, below 10 microns.

Respirable dust is an important, yet often ignored, air pollutant[4].

There are several reasons for concern. Breathable material, typically around 1 micron in diameter, has a high geometric surface area and so has the potential to adsorb hazardous and perhaps toxic substances and to carry these deep into the lungs. An exacerbating fact is that while the larger size respirable dust particles are easily brought into the lungs, they are not easily removed. Harmful material brought into the body by this pathway must be assumed to exert its maximum toxicity.

Several aspects of current attempts at tighter air pollution control further intensify the problem. For one thing, particulate emissions control equipment readily separates out and recovers the larger particles, and with use of electrostatic precipitators removes particles down to about 1 micron. However, this approach loses effectiveness just at the size range of greatest concern for health. Thus, we may well see steadily reduced mass levels of airborne particulates, with greatly improved atmospheric visibility, while at the same time the geographical region of concern may gradually be becoming less healthy because the respirable levels of particulates are increasing.

The projected use of catalysts to clean up auto exhausts has suggested two areas for concern. If the devices contain even small quantities of platinum or any one of many other catalytically active metals, and if the mechanical shaking likely to accompany auto travel leads to significant catalyst attrition loss, airborne particulates may be a source for direct entry of these materials into the body. In many instances toxicity is not well known. Also, effects could be cumulative. Thus prudence dictates a tough attrition loss criterion for acceptance of any automotive exhaust catalyst system, together with research on an urgent basis to establish what risks may actually exist.

A second concern from use of automotive oxidizing catalysts has been that sulfur compounds in the gasoline may lead to early formation of SO_3, and thus sulfuric acid and sulfates, with increased hazard to the population as a consequence. We can quickly make a limiting calculation which should lay this problem to rest. Gasoline to be used with catalyst-equipped cars should have a sulfur content no greater than 0.05 grams per gallon. Further, the vertical mixing height can be taken to be at least a minimum early morning value of 50 meters, and the surface area above which exhaust fumes are dispersed as at least the 10 percent of the basin nearest roadways. Then, using the 120 million vehicle miles per day projected for 1977 without restrictions, we compute that the quantity added each day (whether in the form of SO_2, SO_3, H_2SO_4 or some combination) represents something less than 0.007 ppm. To place this very small quantity in perspective, current Los Angeles APCD alert levels for SO_2 are 3 ppm[5]. It would appear that while use of oxidizing catalysts will speed the chemical change of sulfur in the direction of sulfates, no direct important problem is likely to follow as a consequence.

Automotive use of catalysts is not the only way by which chemically active solid particulate materials enter the atmosphere. An "uncontrolled" fluid catalytic cracking unit; that is, a unit with centrifugal dust collectors but no more effective control equipment in the regenerator exhaust system, can release more than 300 pounds per hour of catalyst dust[6]. The most stringent State or local regulations restrict emissions for the same size unit to about 30 pounds per hour, requiring use of electrostatic precipitators. This is essentially the control level proposed for the future by the Environmental Protection Agency: 0.022 gr/dscf, or 25.7 pounds per hour of particulate matter from a unit rated at 50,000 barrels per day of fresh feed. Cost of this level of control is said to represent only about 0.05 cents per gallon of product. But even low emission levels can lead to significant amounts of catalyst dust in the atmosphere downstream from large petroleum refineries. And such materials could be expected to provide particularly attractive sites by which to transport toxic materials into human lungs. Furthermore, there is the intriguing possibility that in sufficient local concentrations, these catalytically active materials in the atmosphere could alter to some degree the course and speed of atmospheric smog-forming reactions.

A quick calculation can indicate the levels at which we might expect to find cracking catalyst residue in the Los Angeles atmosphere. Using the 1970 value of 928,000 barrels per stream day for the 15 Los Angeles refineries, we assume only 50% cracking and emissions at the 30 pound per hour level for each 50,000 barrel rated capacity. The total of about 3×10^6 grams per day empties into no more than 10 percent of the basin volume, thus into about $5 \times 10^{11} m^3$ assuming no higher than a frequently encountered 500 meter mixing height. This gives an average of about 6 micrograms per cubic meter, substantially below the primary federal particulate air quality standard of 260 micrograms per cubic meter. In this instance, however, we should recognize that very fine point source particulate emissions are carried approximately as a Gaussian plume, not distributed uniformly. Thus we can expect to find areas which are small by comparison with the entire basin, yet miles in extent, over which atmospheric particulates which represent catalyst residue are present in very significant quantities.

The importance of these facts can be emphasized by comparison of the surface areas which may be available from the several sources. Particulate levels observed as an annual geometric mean at the Los Angeles APCD monitoring station nearest major oil refineries are 137 micrograms per cubic meter[5]. If these have an effective 1 micron diameter, these natural particulates provide about 5 x 10^{-3} square meters of surface area within each cubic meter of atmosphere. For cracking catalyst residue we will assume an effective surface area of 500 square meters per gram. Thus cracking catalyst emissions should provide at least about 3 x 10^{-3} square meters of surface area within each cubic meter of atmosphere, on the average, which they contact. This means that the surface areas from these two sources are similar, but the chemical specificity of catalyst residue might make it relatively more important in influencing reactions than ordinary dust. It certainly would appear that research is needed so that we may understand the consequences of releasing this material into photochemical oxidant-plagued atmospheres.

There is one further comparison that at this point is worth making. We have earlier noted concern about attrition loss of catalyst from automobiles to the atmosphere. If in 1977 the Los Angeles car population is catalyst-equipped as has been suggested, a reasonable estimate is that there would be about 1.35 x 10^{10} grams of catalyst contents[7]. Comparing this figure with the 1.1 x 10^{9} grams per year estimate of loss of catalytic cracking catalyst expected even under tight control, we see that this latter figure is equivalent to a mass loss of about 8 percent of the total supply of automobile exhaust catalyst each year. Good mechanical design for automotive systems certainly should preclude loss at this relatively high level. Thus even with good source control, airborne particulates from petroleum refinery operations are likely to remain the larger quantity.

Summary

Three problem areas which follow from environmental restrictions and their relationship to catalysis have been briefly discussed. One problem area, that of liquid refinery wastes, involves technology which is well understood and so represents only a reasonable cost which must be added to any product. The only relationship to catalysis is the fact that added operational expense provides an incentive to seek improved catalysis methods by which to reduce costs, and so offset the added expense. A second problem area, nitrogen oxide emissions from large stationary sources, represents well understood science but emerging technology which has not yet reached petroleum refinery operations. Appropriate use of this knowledge may significantly relax the pressure to reduce nitrogen oxide emissions from other sources. This, in turn, may open alternative pathways by which more flexible and beneficial use of catalysis may be made. A final area, particulate emissions, includes the direct loss of catalytically active material in small but potentially significant quantities to the atmosphere. This represents an area on which research effort should be expended.

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Discussion:

Bailey: What percentage of the energy is lost by going to a black rather than a reflective surface?

Perrine: What is important is how to operate. By burning the fuel one recovers the same total energy. The problem is that the large combustion system has been designed for a certain temperature profile for optimum operation. Operating a little way off may cause as much as a seven percent loss in efficiency. Still, that may be cheaper than some of the other alternatives to control.

Haensel: The catalyst material that's coming out of refineries, if it has a much higher reactivity by a factor of 1,000 or so, would make this difference.

Perrine: People concerned with air pollution have talked about and have worked on aggregation/dis-aggregation of particles, and on the physical processes in their movement. There's also been considerable study of the actual heavy metal content, but I don't think anybody has looked to see whether something could be found that might help solve the basic smog problem.

Libby: Coal fly ash is known to be a good catalyst for coal catalysis.

Perrine: A little shift in some of these reactions could change the sequence of reactions. For example some hydrocarbons are well known to be much more photochemically reactive than others, so that the right kinds of changes could change a whole sequence of reactions.

Holliday: Your point that some of these figures could be misleading is worthwhile repeating, because experiments made of particulate dispersal show that there are enormous variances, and so you may get a dosage many, many times larger than average.

Perrine (Continued)

Perrine: Oh, yes. These are geometric means. The really high values occur when tremendous amounts of dust are carried in from the desert, and that's an entirely different situation. Somebody needs to look at the kind of material released and where it's going. We think it is so little, why worry. But, on the other hand, all concentrations of chemically reactive materials in the atmosphere are small and yet we worry. These low levels are considered by competent health scientists to have a very adverse health effect.

CATALYTIC CONTROL OF CO AND HYDROCARBONS

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It may be perhaps questioned why the Department of Defense should be interested in pollution control and specifically in the control of combustion engine emissions. However, some time ago we had discussions with the Tank Corps, who were bothered by the lachrymators generated by their engines. I think, therefore, from an effectiveness point of view it might be quite helpful to consider air pollution for the Defense Department.

My specific topic is the control of hydrocarbons and carbon monoxide from internal combustion engines both of stationary engines and of the automobile engine. Most of our experience is in the latter area, although we have also done some work with stationary engines, and if I talk mostly about the automotive development, it should be applicable to stationary engines as well.

There is one great difference between the control of combustion by catalytic processes in the industrial field and in the control of exhaust emissions in that in the case of exhaust, we deal much more with transient conditions (frequent acceleration and deceleration), than in the case of normal industrial processes. That adds another dimension to the application of catalysts.

In the engine exhaust, several hundreds of various hydrocarbon compounds have been identified. Slides 1-3 give typical examples: Among the paraffines, major constituents are methane, and larger molecules. Of olefines and acetylenes, major components are ethylene and acetylene. Among the cyclics are primarily benzene and toluene.

In order to develop catalysts for catalytic oxidation one needs some basic information, and I shall review a few of these studies, restricting myself to those which have appeared in the open literature.

The simplest model compound is methane, but it is the most difficult to oxidize. On Slide 4 are data for a number of catalysts(1) such as base metals and palladium and platinum all based on a gamma alumina; palladium is by far the outstanding catalyst for methane oxidation, although platinum has a much lower activation energy, nevertheless, for methane itself, palladium would be the preferred catalyst.

Of various mechanisms which have been investigated for methane oxidation, the one developed by Mezaki and coworkers(2) (Slide 5) in which gaseous methane interacts with adsorbed molecules of oxygen may be the correct one.

Slide 6 shows the rate expression which has been developed based on the proposed mechanism. It is worth noting that the reaction products, CO_2 and water, are both rate inhibiting.

Experimental data in the region of 320 to 380° C (Slide 7) confirm the rate expression developed for this case.

With respect to oxidation of olefins, the sequence of catalytic activity as given in Slide 8 is: platinum, palladium, rhodium, and these catalyst are much better than gold or tungsten(3).

As for base metal catalysts, oxidation behavior of methane and heavier saturated and unsaturated molecules are shown by Slide 9(4), the catalyst being 50% copper oxide on alumina. As a general rule, the longer the chain or the greater the unsaturation, the easier is oxidation, as indicated by the temperature conversion curves. In Slide 10, empirical values are given for the reactions on this catalyst for pre-exponential factors, apparent activation energies and rate constants(4).

Slide 11 is a comparison of the oxidation of ethylene and of propane on palladium, platinum and a number of base metals(5). Platinum and palladium are superior. The fractional reaction orders indicate complicated adsorption mechanisms on the surfaces of the catalysts. Platinum is active at lowest temperature for propane oxidation and palladium for ethylene oxidation.

In the actual engine exhaust it would be very difficult to study catalytic oxidation kinetics of individual organic species. Accordingly, the research group at Mobil Oil of the Inter Industry Emission Control organization have classified the hydrocarbons of the exhaust into two groups: easily oxidized ones, and those oxidized with difficulty (6). Slide 12 shows conversions at various reciprocal space velocities of easily oxidizable hydrocarbons at temperatures from 450-700°F. Agreement with first order reaction rate is poor and holds only at low conversions. The difficultly oxidizable hydrocarbons, at temperatures of 750-900°F conform somewhat better to first order reaction rate (Slide 13). The catalyst employed in this work has not been specified.

Based on these kinetics it has been possible to arrive at activation energies for the oxidation of the two groups which are nearly identical (Slide 14). The significance of measurements of this kind is that they are useful for the design of catalytic converters for exhaust control.

In regard to carbon monoxide, the other major pollutant, the mechanism originally proposed by Langmuir in 1922 for the oxidation on platinum appears to have been confirmed recently(7) (Slide 15). The primary processes lead to a rate expression showing that CO inhibits its own oxidation on platinum. This is significant for so-called closed loop emission control with platinum containing catalysts which will be discussed later on.

The oxidation on base metal catalyst, on the other hand, proceeds as a first order reaction as shown by the Mobil Oil study for the temperature region of 500-900°F(6) as shown by Slide 16. However, compared to platinum, base metal catalysts are inferior.

As to the structure of exhaust control catalysts Engelhard has pioneered the use of monolithic structures. In Slide 17 a comparison is shown between the superficial surface areas of monoliths vs. that of particulate shapes. Monoliths with superficial areas of 2.4 to 3.4m^2/liter are equatable with 1/16 inch diameter pellets but the latter would exhibit a higher pressure drop. It has been demonstrated by General Motors(8) that it is possible to design converters with particulate catalyst beds which possess adequately both sufficiently low pressure drop and sufficient resistance to attrition. However, the use of monolith offers also advantages other than low pressure drop such as flexibility of the mounting attitude.

Engelhard monolith catalysts have been introduced under the designation PTX which comprises a series of types. Slide 18 shows oxidation activity of a PTX catalyst for CO oxidation in the virgin state and after aging at several temperatures.(9) Obviously, thermal aging has a deleterious effect on catalyst activity. The oxidation was carried out in the presence of propane which has no inhibiting effect on CO oxidation. Other hydrocarbons do affect CO oxidation as is shown for another thermally PTX catalyst in Slide 19,(9) ethylene in particular exhibiting a retarding effect on CO oxidation, however, ethylene and CO, if present together, exhibit identical oxidation rates over PTX catalysts.

Slide 20 gives data for a PTX catalyst after actual operation on a vehicle for 50,000 miles using lead sterile gasoline as fuel and ashless oil. The emission value for CO, hydrocarbons, and NOx under EPA-prescribed test conditions (1975 CVS - CH test) were below Federal emission standards for 1975 (currently postponed to 1976) showing that in the absence of poisonous matter aging during 50,000 miles of driving did not cause deterioration to a point that Federal standard could no longer be met(10). Slide 21 provides closer information on catalyst activity decline. Using steady state operation of 30 MPH for evaluation purposes activity for acetylene oxidation had remained unchanged, olefine oxidation had dropped from 99 to 94%, that of aromatics from 99 to 93%. The major decay was for paraffin oxidation from 94 to 37%; methane oxidation, low from the outset, showed relatively little change. With a composite drop of hydrocarbon oxidation from 97 to 81% the vehicle equipped with this PTX catalyst was able to meed Federal Standards after 50,000 miles.

It is of interest to compare catalyst aging during actual operation with thermally induced aging. Slide 22 shows the performance of PTX catalyst after 24 hours steam/air atmosphere aging at various temperatures. The CVS-values for CO and hydrocarbons increase with increasing aging temperature; but even after aging at 1800°F emissions are still below Federal Standards. Quite similar changes in emissions were observed in the mileage accumulation test described before (Slide 23). This study of thermal aging is of considerable value for the development of exhaust control catalysts.

Finally, if the adjustment of the air/fuel ratio of the secondary air injection is such that the exhaust composition becomes stoichiometric or only very slightly oxidizing it is possible to accomplish simultaneously catalytic reduction of NOx and oxidation of CO and hydrocarbons. This requires accurate control of the oxygen content and is sometimes referred as closed loop control. Slide 24 shows performance of a catalyst developed for this type of operation before and after engine aging(11). The stoichiometric point is at an air/fuel ratio of about 14.7. The range at which adequate control of all three pollutants would be feasible is narrow but real. Efforts are underway to develop this technology.

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(3) W. R. Patterson and C. Kemball, J. Catalysis 2 (6) 465 (1963).

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(6) J. C. W. Kuo, C. R. Morgan and H. G. Lassen. SAE Congress Detroit (Mich.). Jan. 1971. Paper No. 710289.

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(10) K. Aykan, W. A. Mannion, J. J. Mooney and R. D. Hoyer, SAE Congress Detroit (Mich.) May 1973 Paper No. 730592.

(11) C. D. Keith, Summary Statement, Engelhard Industries Division, Engelhard, Minerals & Chemicals Corporation, EPA Suspension Hearings on the 1976 Oxides of Nitrogen Emission Standard. June 28, 1973.

Discussions:

Cohn (Continued)

Haensel: I wonder about your way of presenting catalyst surface area based on the actual geometric value. Activity of a catalyst depends on the total surface area, not on the geometrical one.

Cohn: The comparison was primarily for the consideration of pressure drop.

Haensel: You were talking about available surface area. This is what the heading says. In a way that's wrong. The meaningful surface area is what the catalyst offers in total, after all the monoliths are coated and they have a certain surface area. That's what you should really compare rather than the merely calculated surface area. It gives the wrong impression.

Cohn: I referred to superficial area only for the consideration of pressure drop. The monolith has to have high geometrical surface area which then can be developed to a specific area such as 300 m^2/gram or whatever we wish by varying the surface coating.

Hightower: This is a subject that we could spend 2 or 3 more weeks on, and it would be very useful to do so but probably the Department of Transportation would be more interested than the DOD in this particular subject.

PARAFFINS IN AUTOMOBILE EXHAUST

Methane	(Major)	10 - 200 ppm
Ethane		
Propane		
Butanes (n,i)		
Pentanes (n,i)		
Hexanes (n, Methylpentane, Dimethylbutanes)		
Heptanes (n, Methylhexane)		
Octanes (n, Trimethylpentanes)		

1

OLEFINS AND ACETYLENE IN AUTOMOBILE EXHAUST

Ethylene	(Major)	10 - 200 ppm
Propylene		
2 Pentene (Cis, Trans)		
2 Hexene (Cis, Trans)		
Acetylene		10 - 200 ppm

OXIDATION OF METHANE
ON γ-ALUMINA BASED CATALYSTS

Catalytic Component	Reaction Rate (Mols/g.h)·10^2 400°C	450°C	Frequency Factor	Activation Energy Kcals/Mole
Cr_2O_3	17.4	58.8	6.88	23.6
Co_3O_4	10.6	20.5	3.16	12.7
CuO	7.5	23.8	6.15	22.4
MnO_2	3.8	9.8	4.57	18.5
Fe_2O_3	2.2	7.8	6.39	24.8
Pd	486	1,338	7.05	19.6
Pt	215	343	3.27	9.2

Malinsky (1971)

MECHANISTIC MODEL OF METHANE OXIDATION ON PALLADIUM

$$CH_{4(gas)} + 2\ O_{2(ads)} \longrightarrow CO_{2(ads)} + 2H_2O_{(ads)}$$

Mezaki and Watson (1966)

$$r = \frac{LS(S-1)k_{sR}K_{O_2} \times a_{CH_4} \times a_{O_2}^{\frac{1}{2}}}{(1 + a_{O_2} \times \sqrt{K_{O_2}} + a_{CO_2} \times K_{CO_2} + a_{H_2O} \times K_{H_2O} + a_{N_2} \times K_{N_2})^3} \quad (1)$$

Introducing the following stoichiometry of methane oxidation reaction,

$$\begin{aligned} a_{CH_4} &= a(1-x)\pi \\ a_{O_2} &= (b-2ax)\pi \\ a_{CO_2} &= (c+ax)\pi \\ a_{H_2O} &= (d+2ax)\pi \\ a_{N_2} &= e\pi \end{aligned}$$

we derived the linearized form of the rate equation.

$$\sqrt[3]{\frac{a(1-x)(b-2ax)^{\frac{1}{2}}\pi^{\frac{3}{2}}}{r}} = \frac{1}{\sqrt[3]{LS(S-1)k_{sR}K_{O_2}}} + \frac{\sqrt{K_{O_2}}}{\sqrt[3]{LS(S-1)k_{sR}K_{O_2}}}(b-2ax)\pi + \frac{K_{CO_2}}{\sqrt[3]{LS(S-1)k_{sR}K_{O_2}}} \times (c+ax)\pi + \frac{K_{H_2O}}{\sqrt[3]{LS(S-1)k_{sR}K_{O_2}}}(d+2ax)\pi + \frac{K_{N_2}}{\sqrt[3]{LS(S-1)k_{sR}K_{O_2}}}e\pi \quad (2)$$

Mezaki and Watson (1966)

K = ads. equi. constants

L = total conc. of active sites

S = Number of equidistant active sites (centers) adjacent to each other

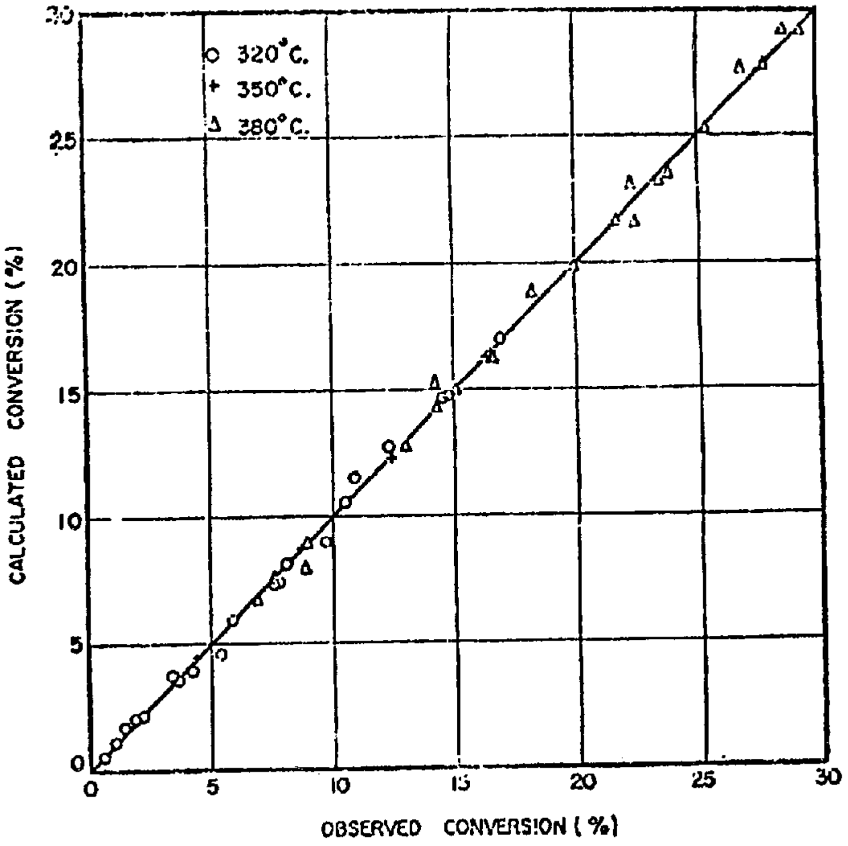


Figure 2. Observed and calculated values of conversions

Mezaki and Watson (1966)

RELATIVE ACTIVITY FOR OLEFIN OXIDATION

Pt > Pd > Rh >> Au > W

Patterson and Kimball (1963)

Moro-Oka, Morikawa and Ozaki (1967)

TABLE 3

KINETIC PARAMETER OBTAINED IN ETHYLENE OXIDATION

Catalysts	Reaction orders in ethylene	Reaction orders in oxygen	Temperature range (°C)	E (kcal/mole)	log A (A in mole/m² sec)	log V_{30} (V in mole/m² sec)
Pd	—	—	174 ~ 195	26.6	5.95	−4.23
CuO	0.39	0.27	238 ~ 282	24.5	4.12	−6.86
Co_3O_4	0.14	0.21	200 ~ 251	30.5	7.32	−5.93
NiO	0.38	0.39	268 ~ 316	26.3	4.05	−7.63
MnO_2	0.52	0.34	229 ~ 279	19.6	2.91	−6.21
Fe_2O_3	0.58	0.47	280 ~ 320	29.3	5.04	−7.77
Cr_2O_3	0.60	0.30	240 ~ 292	27.7	5.13	−7.07
CeO_2	0.67	0.32	342 ~ 395	24.4	1.45	−9.48

TABLE 4

KINETIC PARAMETER OBTAINED IN PROPANE OXIDATION

Catalysts	Reaction orders in propane	Reaction orders in oxygen	Temperature range (°C)	E (kcal/mole)	log A (A in mole/m² sec)	log V_{30} (V in mole/m² sec)
Pt	0.83	−0.09	220 ~ 260	17.0	1.39	−5.09
Pd	1.3	−1.6	337 ~ 368	36.3	6.89	−6.09
CuO	0.54	0.16	309 ~ 363	28.7	3.83	−7.13
Co_3O_4	0.94	0.30	275 ~ 311	24.5	2.58	−6.76
NiO	0.89	0.40	350 ~ 416	26.2	1.68	−8.33
MnO_2	1.01	0.00	294 ~ 358	28.3	3.80	−7.01
Fe_2O_3	0.68	0.22	395 ~ 425	35.9	4.87	−8.83
Cr_2O_3	0.78	0.17	283 ~ 341	21.9	1.47	−6.88
CeO_2	0.67	0.25	383 ~ 450	27.8	1.41	−9.21
ThO_2	—	—	373 ~ 418	36.8	4.65	−9.26

NOT REPRODUCIBLE

Table II. Empirical Reaction Rate Parameters

Hydrocarbon	*A, Mole/ G.-Sec.-Atm.^{n}*	*E, Cal.*	*n*
Methane	5.53×10^2	23,000	0.9
Ethane	9.20×10^3	26,000	0.7
Ethylene	5.82×10^1	18,000	0.5
Acetylene	6.67×10^2	19,000	0.2
Propane	1.26×10^1	17,300	0.6
Propylene	6.58×10^1	17,500	0.5
Propadiene	4.44×10^0	15,000	0.3
Propyne	4.15×10^0	17,000	0.0
Cyclopropane	2.12×10^1	16,000	0.8

Nobe and Accomazzo (1965)

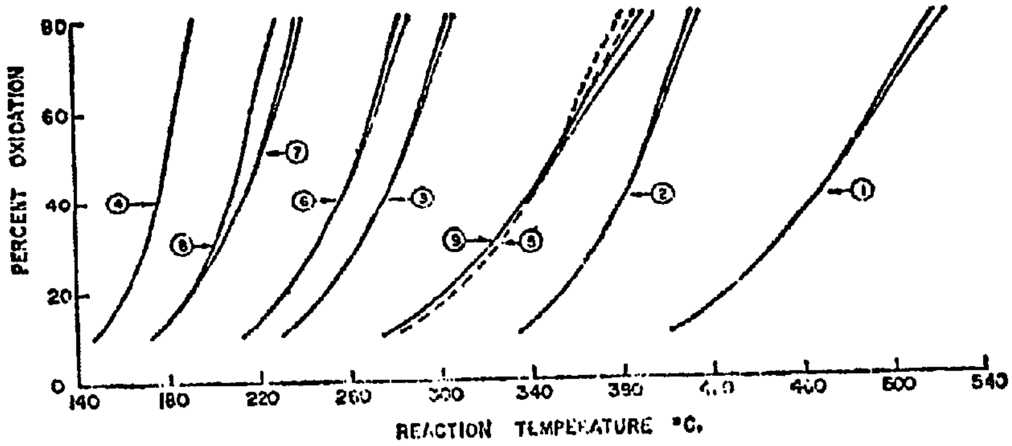


Figure 6. Comparison of catalytic combustion of C_1 to C_3 hydrocarbons

Flow rate = 525 liters/hr. Initial concentration = 500 p.p.m.

1. Methane
2. Ethane
3. Ethylene
4. Acetylene
5. Propane
6. Propylene
7. Propadiene
8. Propyne
9. Cyclopropane

Nobe and Accomazzo (1965)

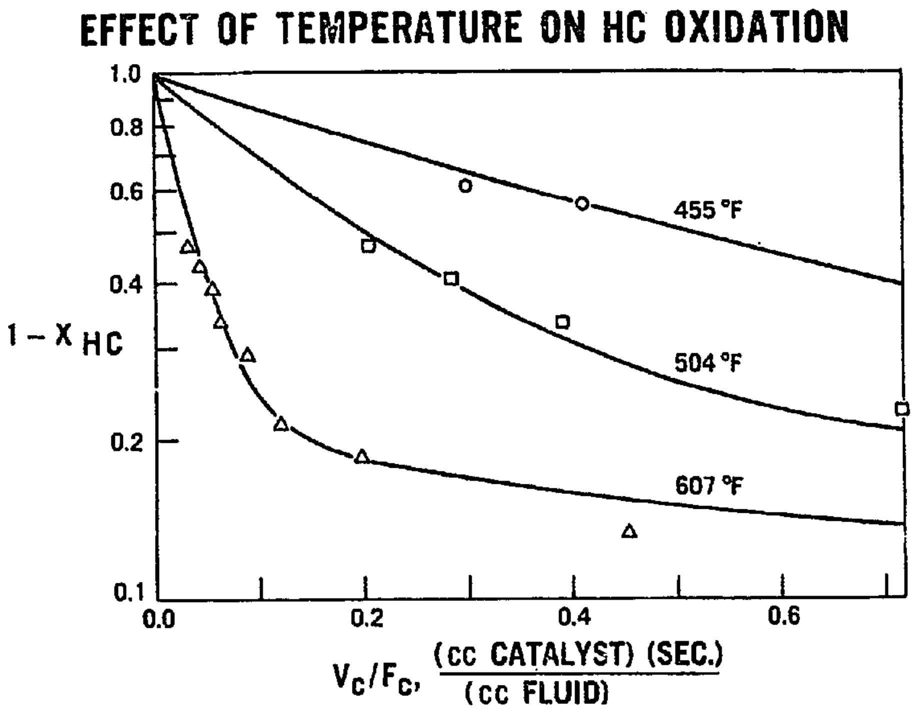
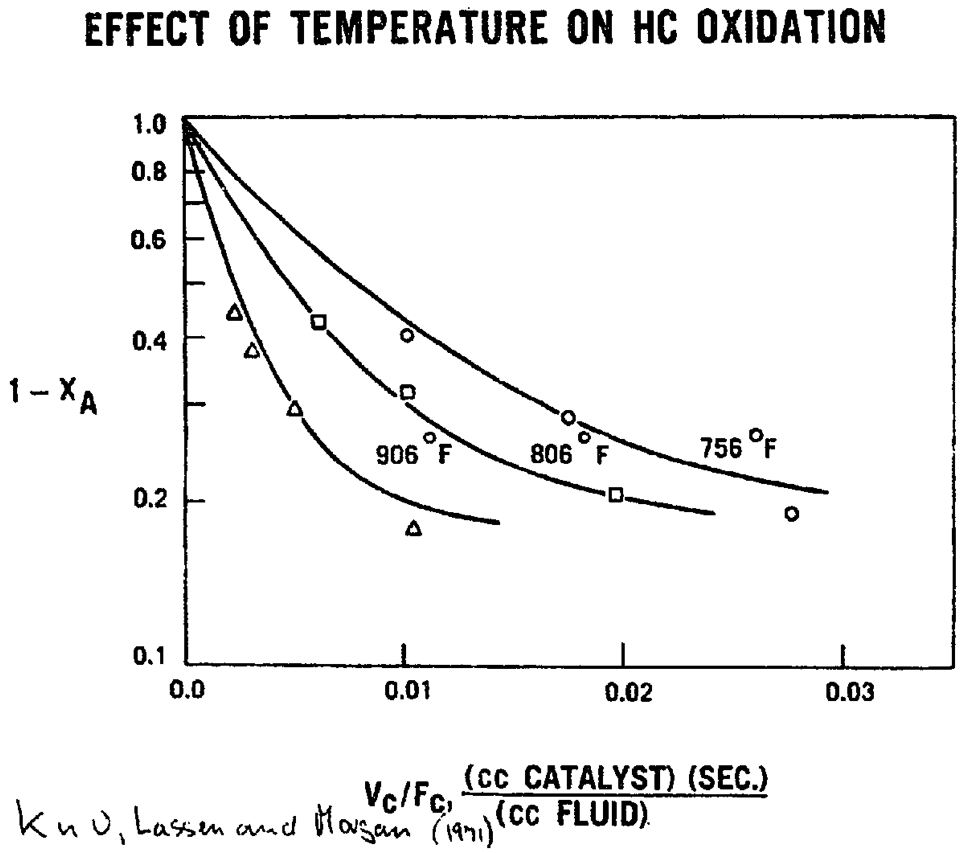


Figure 12

14

Ku O, Lassen and Morgan (1971)



Ku O, Lassen and Morgan (1971)

194

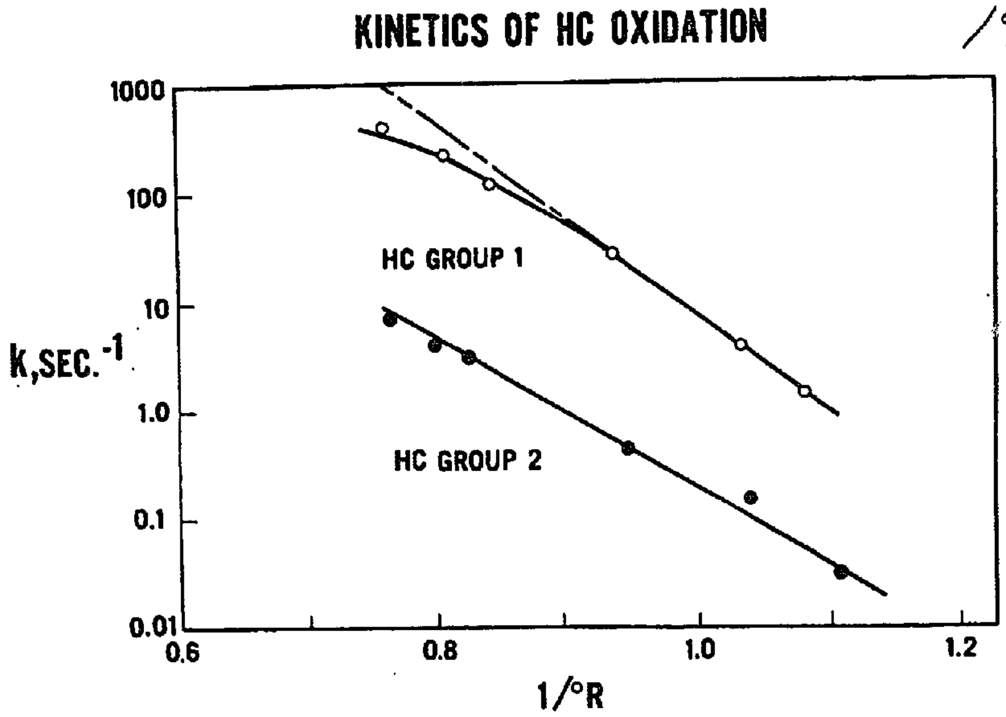


Figure 14

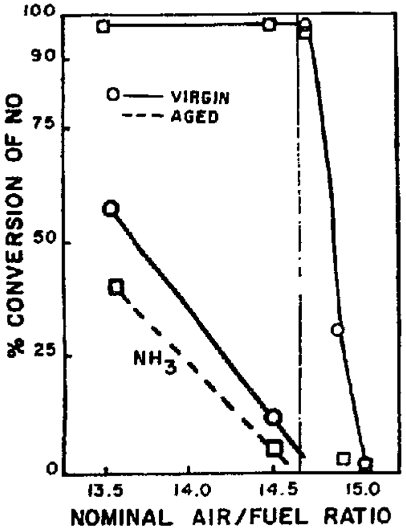
Kuo, Lassen and Morgan (1971

Comparison of Superficial Surface Area

		METER²/LITER
Monolithic	7/8 Corrugation/in.	2.35
	10 Corrugation/in.	3.42
	20 Corrugation/in.	4.63
Tablets	1/8 D x 1/8L — Flat Heads	1.11
	3/8 D x 3/8 L — Flat Heads	0.46
Spheres	1/8 Dia.	1.27
	1/4 Dia.	0.48
Extrudate	1/16	2.53
Rings	1/2 D — 3/16 Holes	0.46
Coated Wire	Demister Mesh w/ Al_2O_3 Coating	0.50

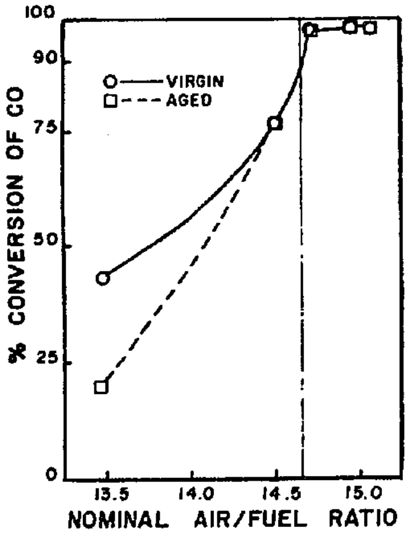
FIGURE V

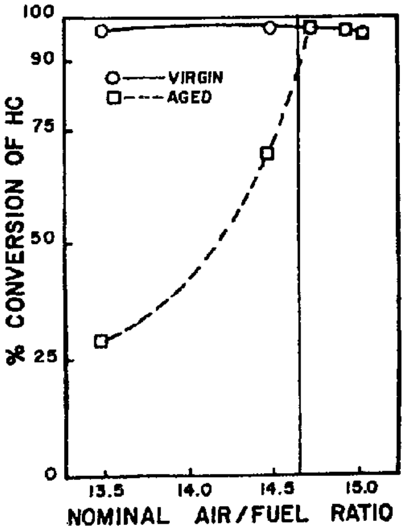
ENGELHARD TWC-I CATALYST



TEST CONDITIONS
TEMPERATURE 650°C (1200°F)
VHSV 100,000

AGING CONDITIONS ON DYNAMOMETER
INLET TEMPERATURE 760° C (1400°F)
FUEL Lead sterile
TIME 60 HOURS, 10% Oxidizing (15/1)





OXIDATION OF CO ON PLATINUM

Probable Primary Steps

$$CO_{(ads)} + 1/2\ O_{2(gas)} \longrightarrow CO_{2(gas)}$$

$$CO_{(gas)} + O_{(ads)} \longrightarrow CO_{2(gas)}$$

Rate: $$\frac{d\ CO_2}{d\ t} = k \frac{p\ (O_2)}{p\ (CO)}$$

Langmuir (1922)

Heyne and Tompkins (1966)

CYCLICS IN AUTOMOBILE EXHAUST

Benzene	(Major)	5 - 50 ppm
Methylcyclopentane		
Toluene	(Major)	10 - 100 ppm
Xylenes (o, m, p)		
Ethylbenzene		
Propylbenzene, Methyl ethyl benzene, Trimethylbenzene		
Butyl benzenes		

EFFECT OF TEMPERATURE ON CO OXIDATION

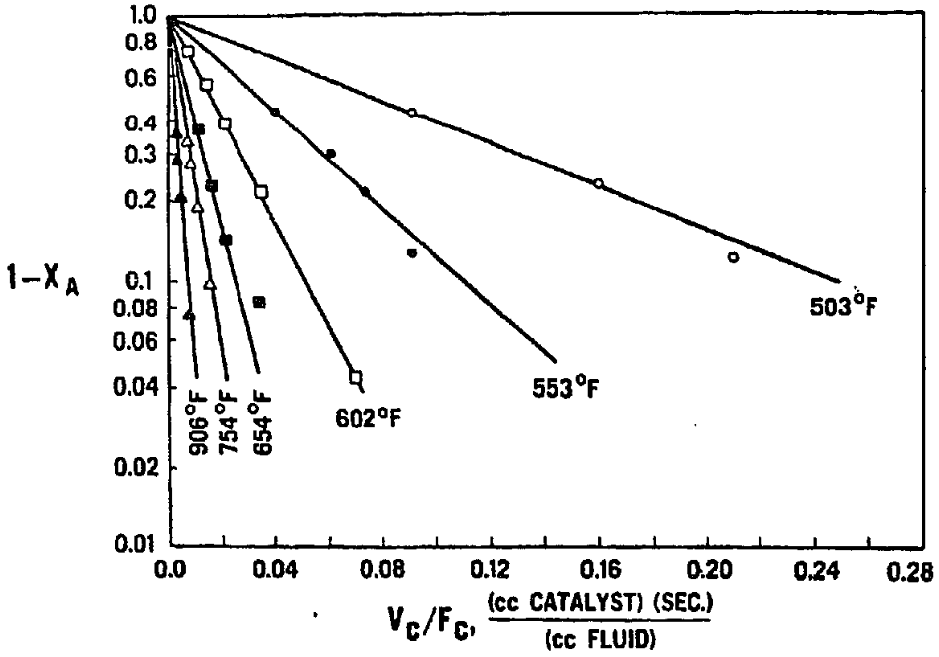


Figure 9

10

Kuo, Lassen and Morgan (1971)

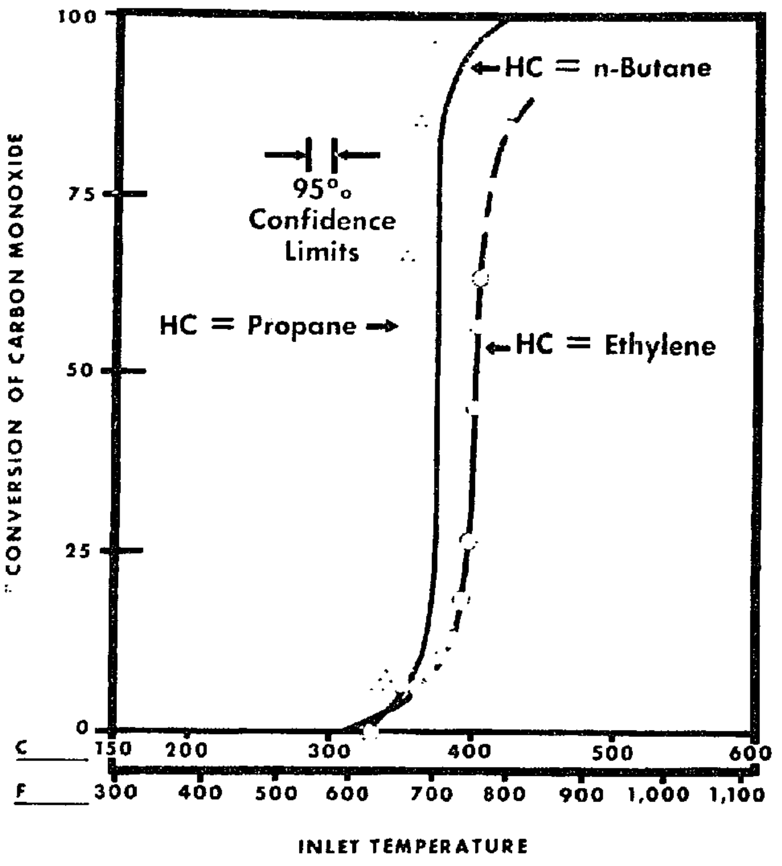
STANDARD PTX

INDIVIDUAL EFFECT OF HYDROCARBONS ON ACTIVITY OF HEAT TREATED CATALYST FOR CO OXIDATION

(After heat treatment in air 24 hrs. at each temp. 1400 + 1600 + 1800 F)

Catalyst Volume = 1½ dia x 3" long monolith or 90cc pellets

VHSV = 40,000 Hr-



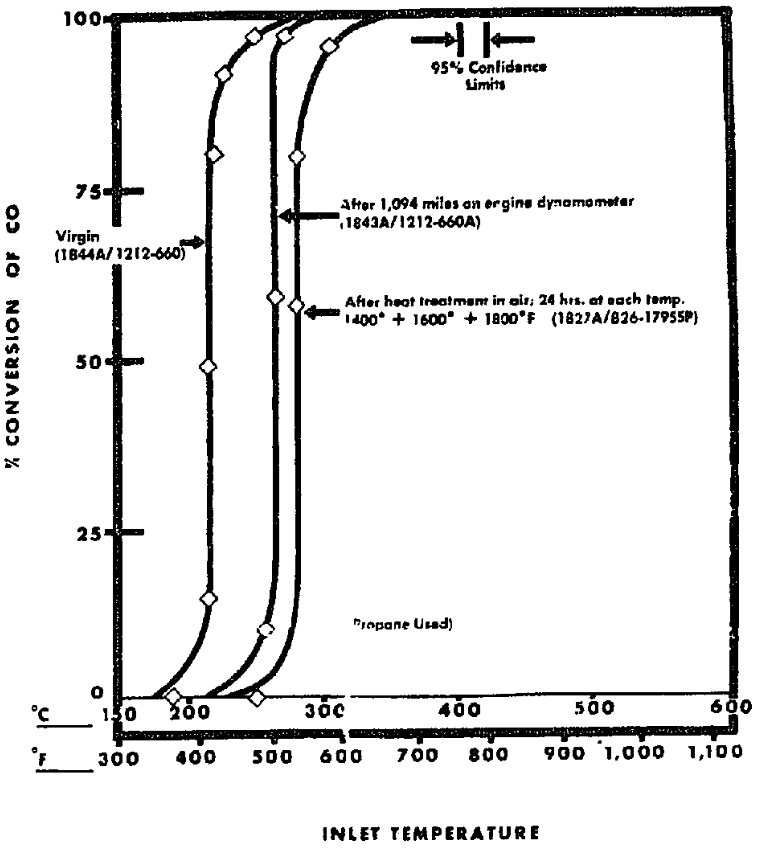
IMPROVED PTX

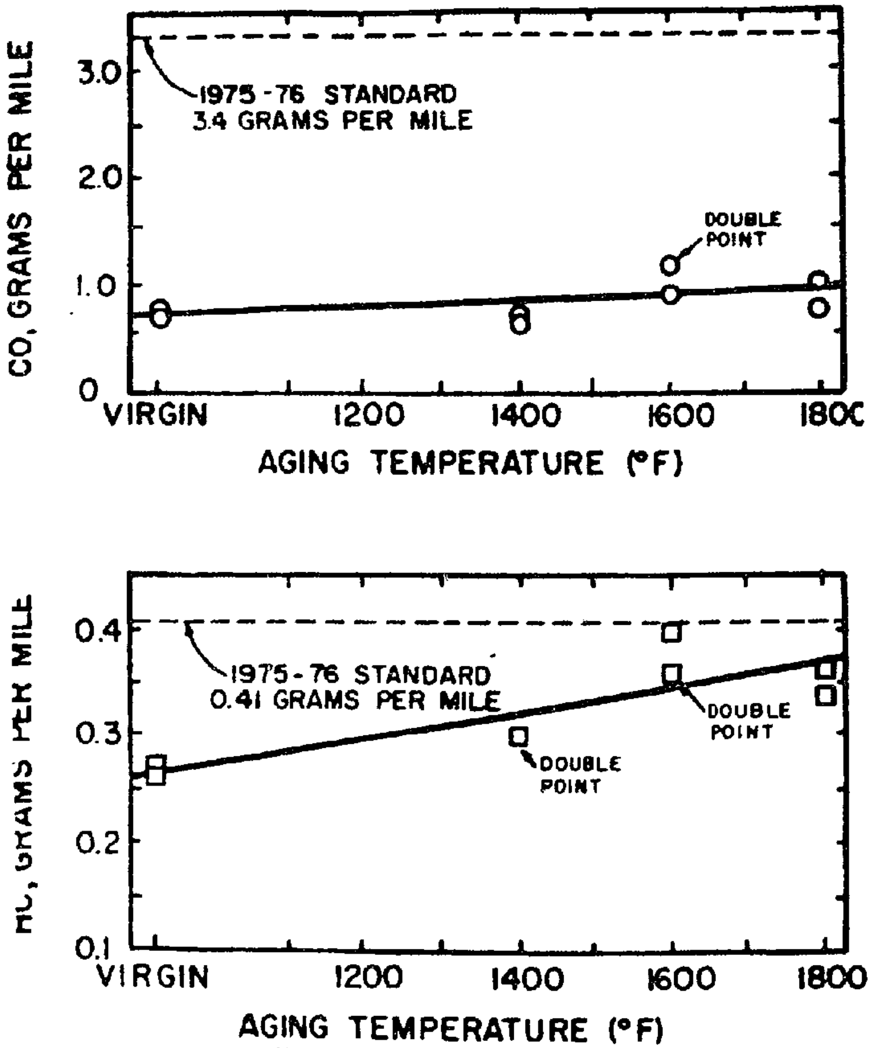
FIGURE 9

EFFECT OF AGING ON ACTIVITY FOR CO OXIDATION

Catalyst Vol. = 1½" dia. x 3" long

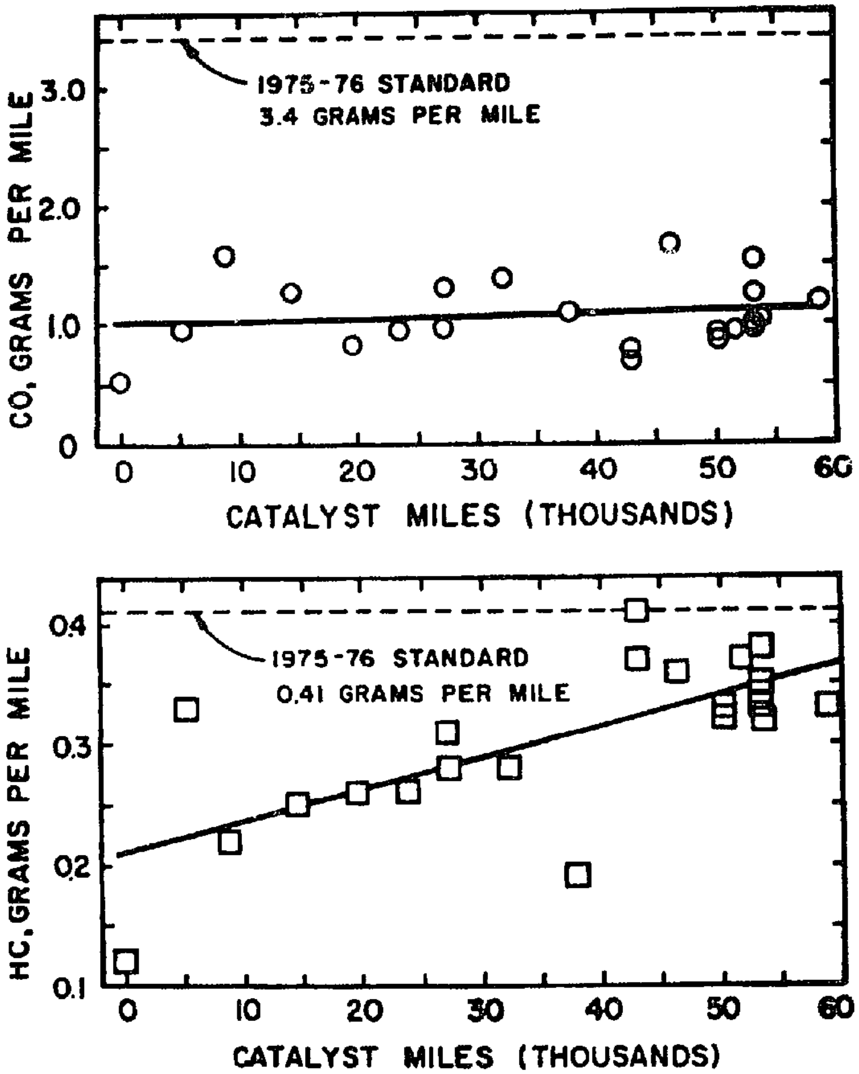
VHSV = 40,000 Hr-1





Effect of 24 hours Laboratory Steam/Air Aging of PTX Type IIB Catalyst on 1975 CVS Test Performance

21



Vehicle Durability Test of PTX Type IIB Catalyst (1975 CVS Tests)

22

PERFORMANCE ON PTX TYPE II B CATALYST AFTER 50,000 CATALYST MILES ON VEHICLE

1975 CVS TEST

GRAMS/MILE

HC	CO	NOx
0.36	0.92	2.89

1975 U.S. FEDERAL STANDARDS

0.41	3.4	3.0

TEST RESULTS* SHOWING CONTINUED REMOVAL OF OLEFINS AND AROMATICS AFTER 50,000 MILES

	FRESH PTX (After 500 Miles)	AGED PTX (After 50,000 Miles)
SMOG PRECURSORS % Removal Of Hydrocarbons		
ACETYLENES	100.0	100.0
OLEFINS	99.1	93.7
AROMATICS	99.1	93.4
OTHER HYDROCARBONS		
OTHER PARAFFINS	93.9	36.8
METHANE	11.3	9.6
TOTAL HYDROCARBONS (CARBON BASIS)	97.1	81.4
Decrease in Total Reactivity of Emitted Hydrocarbons	99.2	91.9

*Steady State 30 MPH

NO_X REMOVAL FROM EXHAUST GASES

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Klimisch: I'll try to restrict myself to stationary sources. As yet catalytic removal of nitrogen oxide from exhaust gases from stationary sources hasn't attracted a great deal of attention, because there are simpler means of controlling nitrogen oxide emissions namely to prevent its formation in the first place. These methods generally involve some technique to minimize peak combustion temperatures and generally don't involve a great loss in efficiency. However, as emission standards become more stringent, catalytic methods may be given more attention.

The basic problem with NO removal is that we don't know how to reduce NO in oxidizing atmospheres. Most combustion processes are carried out with an excess of air. For example, coal is generally burned with 15 or 20% excess air; if the excess is less, there are coking problems. The only way to generate a reducing environment is to use some other fuel, perhaps a clean fuel like natural gas, and there are obvious objections to doing this. The first slide shows the exhaust gas composition from various kinds of combustion processes. First of all there are large excess of air in coal and oil exhausts. Gas can be burned anywhere. The mixing ratio for the internal combustion engine can be varied widely. The SO_2 levels in the internal combustion engine are about 10 times lower than SO_2 levels in combustion of coal and oil, whereas nitrogen oxide levels are reasonably constant for all these combustion processes. This sulfur is of concern for two reasons. One is that in most catalytic processes it's a poisoning problem to the catalyst.

Klimisch (Continued)

Also it is a more difficult and serious air pollution problem than are nitrogen oxides in all except the automotive case. We didn't think we had a sulphur problem, but there are hearings going on in Washington this week which will apparently decide that. In any case, there are some combination methods that presumably remove both sulfur oxides and nitrogen oxides and most of those involve some system to generate a reducing atmosphere which tend to waste fuel.

Another place where NO removal is perhaps of DOD interest, is in nitric acid plants, where explosives are made from nitric acid and so perhaps the control of NO emissions from these kinds of plants are of interest. This kind of technology has been available for some time. You can use a variety of catalysts and a variety of reducing agents, and there is no real sulfur problem. There is the excess oxygen problem and ammonia has been mentioned as a selective reducing agent for the NO emissions, but perhaps no great deal of research attention is needed.

For controlling NO emissions from installations that involve automotive type engines, there's probably been sufficient technology developed already. This can be accomplished to a large measure by mechanical means, like exhaust gas recirculation, which really doesn't cause loss of efficiency. And, in addition for a steady state operation, perhaps one can accomplish control of all three pollutants quite easily. I think that the technology is available. People from UOP have presented information on that a variety of times. For other types of engines such as turbines or diesels, catalytic treatment is very difficult because these engines operate with large excesses of air, and more research is needed for getting rid of NO in oxidizing atmospheres catalytically.

Klimisch (Continued)

I don't think anybody's very optimistic about being able to do that but it's very intriguing because NO is thermodynamically unstable so that theoretically it is possible to convert NO to nitrogen. There has been some interesting work by Professor Boudart's group among others on that particular reaction and considerable work planned for US-USSR interchange. Actually, it's even difficult to get nitrogen unfixed in a reducing environment, and that's what we've been facing in the automotive problem. Although there's been a great deal in trying to reduce NO emissions, it hasn't yet been successful and perhaps it won't be used, although the way the law stands we still think we are going to have to go that way.

The next slide shows basically what we found in all that work. There are two kinds of catalysts for reducing NO; ruthenium which takes NO to nitrogen and then there's all the catalysts which appear to take NO to ammonia. Most of those get to nitrogen by subsequently decomposing the ammonia. Some of this nitrogen catalytic chemistry may be of interest to the DOD for other reasons, perhaps for propellant decomposition. Hopefully there will be some useful fallout from all this research effort on automotive catalytic control.

The next slide shows a variety of reactions that NO can undergo. Generally, when you try to reduce NO you get all three products, N_2O, N_2 and NH_3 depending upon the conditions.

In conclusion, stationary control of NO in exhaust gases by catalysts is not very promising because of the excess oxygen used. The NO catalysis, however, is of extreme chemical interest. The NO molecule is an interesting and unusual and often perverse molecule and it's quite useful to probe surfaces with.

Klimisch (Continued)

There is the faint hope of being able to decompose NO in oxidizing atmospheres. There is presumably some interest in propellant decomposition by catalyst. There is a possible interest in corrosion, although generally in combustion processes the sulfur causes a lot more problems than do the nitrogen oxides. We're obviously interested in those kinds of high temperature corrosion processes, and I know that the DOD is also quite interested. For example, the problem of sulfidation of turbine blades is costly and troublesome for the Navy. But the interactions of sulfur with catalysts is a constant threat to the use of catalysts. I'm sure more attention and time and research money, will be spent on this threat.

Hall: I'd like to ask Dick why he feels so pessimistic about NO reduction by ruthenium catalysts.

Klimisch: As yet we haven't seen any indication that ruthenium has the required stability or durability for the automotive application. Besides there's the problem of ruthenium availability. Platinum is of the order of a 10th of an oz per ton in the ore. Ruthenium is an impurity in platinum as you know, and there are a lot of automobiles made.

Hall: So there is certainly here a problem of catalyst improvement.

Klimisch: Yes, there certainly is.

$$NO \xrightarrow{\hspace{4cm}} N_2 + (O)$$

1 a

VOLUME PERCENT OF

EXHAUST GAS CONCENTRATIONS

	COAL	OIL	GAS	I.C.E.
O_2	3.30	3.0	2.0	0.3 - 2
SO_2	0.20	0.15	-	0.002
NO_X	0.07	0.07	0.07	0.07

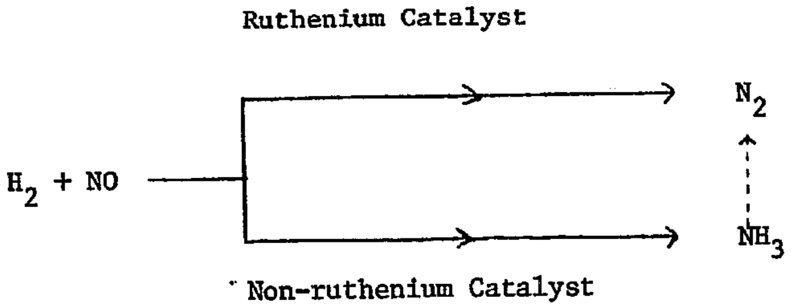
1 b

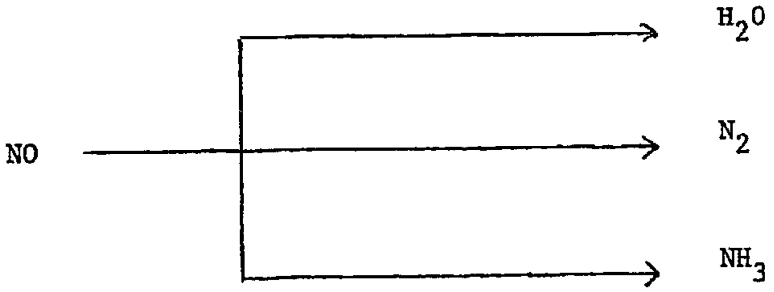
NITRIC ACID PLANT; NO CONTROL

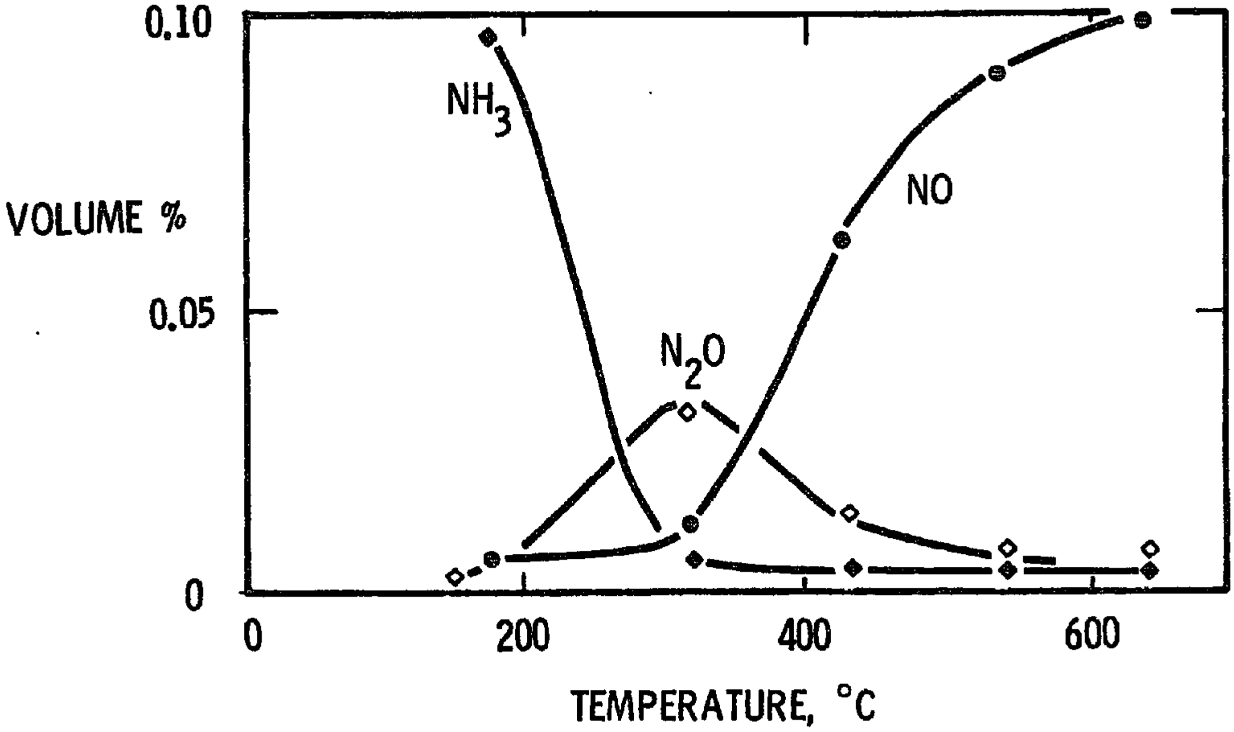
Catalyst: Pt or Base Metals

Gases: CO, K_2, CH_4, NH_3, Excess O_2

No Sulfur







FEEDSTREAM = 0.090% NH_3, 0.90% CO,
2.0% O_2, BALANCE N_2
GHSV = 15,600

FIGURE 3 - THE CATALYTIC OXIDATION OF AMMONIA OVER A 1% PT ON Al_2O_3 CATALYST.

CONTRIBUTIONS OF SURFACE STUDIES TO CATALYTIC REACTIONS

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I shall talk about some clean surface studies we have been carrying out to understand hydrocarbon catalysis on platinum. We are discussing here the art of catalysis and I'd like to convince you that there is a glimmer of hope that we can convert that to the science of catalysis if we work hard enough, and if the needs of technology improves fast enough to provide the incentive to do more basic research. The techniques that have been developed in the past ten years allow us to look at the atomic structure, composition, and detailed nature of chemical bonds of surface adsorbed species. With these fundamental informations all the applied areas of chemistry will flourish. By making the connection between the phenomena one observes, the structure and the composition, it should be possible to develop a good mechanistic picture of catalysis on an atomic scale. Let me describe some of our studies on platinum surfaces, and then demonstrate similar principles that one might expect to operate on alloy catalysts. Figure 1 is a schematic representation of a surface with all the various atomic species. Catalysts work for thousands of hours so that one can more or less disregard non-equilibrium species. Atomic steps and atoms in terraces are very stable, thermodynamically. The ad-atom concentration is less than 1% even near the melting point and so are the concentrations of vacancies.

Low energy electron diffraction from the (111) platinum surface (platinum is face centered cubic, and the (111) surface is the densest plane), shows that the surface has the structure that you believe it should have (Figure 2).

This is obviously one of the crystal faces that must be present in catalytic reaction, since it is the crystal plane with the lowest surface energy.

If a crystal is cut at different degrees off the (111) crystal face by slicing it, it exposes high Miller index surfaces. This one, Figure 3, was made by cutting it at 6° off the (111) face, and is characterized by a step structure. The diffraction picture indicates a very well defined periodic arrangement of steps, separated by terraces nine atoms wide on the average (there are many terraces of seven or six atoms wide up to ten atoms wide). If one cuts at a steeper angle the surface has a very well defined diffraction pattern indicating the presence of (111) orientation terraces separated by steps of four atoms wide.

The next slide, number 4, shows that you can cut a surface, instead of along crystallographic zones, in a skewed manner, forming steps of high Miller indices that define surfaces with a very high density of kinks. Now all of these crystal faces show a remarkable thermal stability, stable to more than a thousand degrees centigrade. They do not recrystalize nor facet in any way under temperatures at which normal catalytic, hydrocarbon reactions take place on platinum. So all of these crystal faces are probably present on a small particle of 15 to 50 Ångstroms in diameter. For a 15 Ångstrom particle, roughly 30% of the atoms must be in step positions. At 50 Ångstroms or so, it is reduced by an order of magnitude. So both atoms in step position and in terrace positions must be present on small catalyst particles. What I'm trying to do is by studying the reactivity of single crystal surfaces of well defined atomic structures to understand the reactivity of small catalyst particles and their structural behavior.

One of the techniques that has been developed lately is the scattering of molecular beams from surfaces. Slide 5 shows schematically this technique. Using a mass spectrometer that rotates, one measures the angular distribution of the product. If you chop the incident beam and measure flight times, you can measure residence time of the molecule on the surface. By chopping the scattered beam from the flight time, one measures the velocity of the scattered product. So this measures energy transfer between reactants and the surface.

If one scatters a mixture of H_2 and D_2 from a low index face, no detectable amount of HD is formed. However, with a step surface where the step orientation and the low index face are both (111) with 9 atom wide terraces, about 10 to 15% HD forms. If there are impurities like CO on the surface the residence time of HD increases remarkably, with corresponding increase in the reaction efficiency. These studies may help to uncover the mechanism of this simple reaction but we are also interested in more complex reactions. Slide 6 will show how we studied those at low pressures, using a vacuum chamber at a reaction pressure of about 10^{-4}, 10^{-5} Torr and a mass spectrometer. We can use one face of a single crystal at any orientation, and those that I showed are examples of these different orientations used to study the product distributions in all sorts of complex hydrocarbon catalytic reactions. Here we used a low energy electron diffraction chamber to look at the surface structure before and after catalysis and sometimes even during, if the pressure is low enough. We use Auger spectroscopy to measure the surface composition and mass spectrometry to measure the product distribution. The sensitivity is adequate to measure low probability chemical reactions from one face of a crystal of less than a square centimeter in area.

Slide 7 details the n-heptane→toluene reaction, the reaction that we have studied mainly up to now, although we have also studied the cyclohexane→cyclehexene→benzene reactions. This takes place selectively on platinum. The conditions we utilized in our studies are not far removed from industrial conditions, except for being something like eight orders of magnitude lower in pressure, and that is a long way to extrapolate.

Slide 8 shows turnover number, that is number of toluene molecules formed per platinum atom per second, as a function of a series of crystal planes all of which were cut along the same crystallographic zone. The only difference is the terrace width which is always increased by one atom, but the orientation is the same. One finds remarkable inactivity for this sort of reaction for all but one or two of the crystal faces that have terrace widths of about 5 or 6 to 7 atoms wide. Remarkably, however, when you form these terraces there is the onset of formation of ordered carbonaceous deposits on the surface which can be identified as due to partially dehydrogenated carbon deposits. The catalytic activity is associated with the presence of these ordered carbonaceous layers. We have not been able, on any of these catalysts at these low pressures, to obtain chemical reaction without the presence of these ordered carbonaceous layers. So I tend to believe that they play a very important role. In fact, most likely what acts as a catalyst is not the platinum itself but platinum plus the partially dehydrogenated adsorbed layer on the surface. Slide 9 shows the conclusions of a large number of studies (which will be published in Surface Science in January 1974). These various crystal faces exhibit all the richness of chemistry one encounters on catalyst particles. Certain crystal faces show dehydrogenation behavior dominantly, while others, like this highly kinked surface break carbon-carbon and carbon-hydrogen bonds non-selectively. Still other surfaces don't seem to be very catalytic for this n-heptane→toluene reaction.

Now a structure sensitivity of this reaction has been predicted by others, for example by Professor Boudart and his group, and we can confirm this. It is clear that we can optimize catalytic activity by creating an optimal atomic surface structure, with a corresponding increase in rate by about a factor of 20 or so. Perhaps other crystal orientationsmay be much better than these which we have studied.

I think that an ordered carbon structure on the surface plays a very important role, at these low pressures. I conjecture that this is an example where heterogenerous catalysis simulates enzyme catalysis, that the more complex the chemical reaction that is taking place, the more likely that it takes place by poisoning other reactions by putting on the surface a certain structure that will only catalyze the reaction of a molecule of a certain shape or certain geometry and will reject all other reactions. I think, to a large extent, selectivity and poisoning mean the same thing. In this case we are inhibiting hydrogenolysis and other bond-breaking processes and enabling this complex dehydrocyclization reaction of rather low probability to dominate. These carbon structures and how they affect various chemical reactions is our study for the future and in the present as well. That eight orders of magnitude difference of pressure bothers me and so we are trying to measure the same catalytic reaction process at atmospheric pressure. Those of you who went to the California Catalysis meeting heard Dr. Kahn speak, whose Ph.D. thesis I am presenting here in one minute. This is the catalytic chamber, Figure 10, that withstands both ultra high vacuum as well as high pressure. A gold sealed reaction chamber containing a well stirred reactor here allows us to study on the same crystal face various catalytic reactions. The one Kahn studied was the cyclopropane ring opening, to calibrate our technique.

Slide 11 shows the rate of production of propane per square centimeter of platinum and the next slide, number 12, shows how these rates are converted into turnover numbers. The important thing is that the poly-dispersed rates are within a factor of two the same as from catalysts by a single crystal of small area. The agreement indicates that the cyclopropane ring opening is a structure insensitive reaction. If it had any structure sensitivity, probably the rates wouldn't at all be the same. Also it is clear that one can measure catalysis under atmospheric conditions on one face of a single crystal. Why should one do that? Because on such a crystal one can determine the chemical composition of the surface by Auger spectroscopy and the atomic structure by diffraction, and one can establish the correlation between catalytic activity and these fundamental parameters. Slide 13 I am borrowing from Sinfelt. The surface structure of platinum doesn't tell the whole story of the catalytic activity of platinum because gold has the same crystal structure and we all know that gold dust is a very poor catalyst. By changing the number of d electrons, one can change the catalytic activity by orders of magnitude. One way of learning why platinum is a good catalyst is to study gold and find out why it isn't. Clearly, studying variation of catalytic activity along the periodic table is an important research tool. We can also study alloys and the surface composition of alloys and I am showing again one of Sinfelt's studies, Figure 14, in which he followed the hydrogenolysis of ethane on ruthenium-copper catalyst and osmium-copper catalyst and found that changing the alloy composition changes the reaction rate by orders of magnitude. The next slide, number 15, shows the Auger spectrum of a lead-indium alloy of about 24 atom percent lead. The relative intensity of a given indium Auger peak and a lead peak measures the surface concentration of lead and the surface concentration of indium on a precalibrated system, and shows that the surface composition is not equal to the bulk composition. These Auger studies allow determination of the monolayer composition as proven by some of Boudart's and William's studies as well.

For solid solutions we can show Figure 16 which shows that the surface atom ratios of the two components are related to the bulk atom ratios by an extremely strong exponential dependent on the surface tensions, surface free energies of the pure components, and the temperature. While the bulk component is temperature independent, the surface components are temperature dependent, the surface ratio composition is temperature dependent, and the surface is exponentially enriched in the component of the lower surface free energy. For a regular solid solution, the same arguments apply except there is a regular solution parameter which very interestingly varies the second layer composition with respect to the first layer composition. The surface composition may be very different from the bulk composition. Of course, when a hydrocarbon is adsorbed instead of the surface free energy of the two components what matters is some interfacial energy between adsorbed carbon and the metal. And, of course, if the interfacial energies are the same, if carbon forms the same strength bond with the two metal components of the solid solution then the surface and the bulk ratios will be the same. However, this is rarely the case. For example, for a silver-palladium catalyst, if carbon monoxide is adsorbed on the surface, the palladium is pulled to the surface, whereas normally silver would be in excess on the surface. Slide 17 shows the surface free energies can be predicted from the heats of vaporization and this is rather important because surface tension measurements are difficult to perform, and in fact on solids it is almost impossible to obtain reliable data.

Auger spectroscopy tells not only how much of one or the other components are on the surface, but also what's the valency, what's the oxidation number.

Slide 18 shows that for an Auger transition in vanadium for various vanadium oxides, there is a chemical shift of about 0.6 volt per oxidation number. The uncertainty in the energy resolution is about 0.1-0.2 volts, so that one can easily distinguish between bulk oxides and what is on the surface. Vanadium pentoxide in the bulk does not necessarily mean that there is venadium pentoxide on the surface. There are some very nice studies from Belgium by Fiermans and Whennick that indicate that a reduced vanadium pentoxide exists on the surface and there is an instant oxygen evolution if bulk vanadium pentoxide is cleared to create new surfaces.

Another type of catalyst is the one studied by both Henry Wise and Professor W. F. Libby. Namely for metal oxides one can vary the surface stoichiometry and titrate in the oxidative power of certain reactants. In this case it is propylene being oxidized to acroleine (Figure 19), but beyond a certain oxide composition actually the oxidation goes too far and propylene is oxidized all the way to CO_2. Both for the copper oxides and for the perovskites the stoichiometry of the surface may be titrated to custom tailor selective catalytic reactions. From the talk of Dick Klimisch, it is clear to me that an oxide might actually reduce NO in the presence of an oxidizing atmosphere whether it is a cobaltite or uranium dioxide or other. Such an approach, varying the surface composition to carry out selective surface reactions, may be very fruitful, and can be thoroughly understood because using Auger spectroscopy we can determine both the composition and the oxidation state of the surface before and after the catalytic reaction, so we can follow what's going on.

I'd like to emphasize the following points in conclusion. We have a lot of work to do designing prototypes of catalyst particle structures using the properties of the single crystal surfaces. In this way we may be able to select various catalytic properties and optimize them. One can measure catalytic properties of very small surface area crystals, and one can actually bridge the pressure gap here; I think that these studies should be continued. Because alloy catalysis is such an important part of hydrocarbon catalysis, one should take note that the surface composition may be very very different from bulk composition. Thank you very much.

Discussion:

L. Libby: Do you recommend this non-stoichiometric surface study then for continued research in catalysis?

Somorjai: Very much. In fact, at this stage, with an investment of about $5,000 for a cheap Auger spectroscope, people should look at their catalysts and measure the surface composition. A tremendous amount of information could be gathered by simply looking at what's on the surface. When you say you have a molybdenum catalyst, you don't really mean that; you mean that you have a catalyst with a molybdenum sulfide or a molybdenum-hydrocarbon surface which may have a composition very different from molybdenum. In our search for future new catalysts, it is very important to define what is on the surface.

Worley: Using low energy electron diffraction to study for example a surface with six atom wide terraces what percentage of that surface might be something else besides 6 to 1?

Somorjai: We can determine two things. From the spot size we can determine the distribution of terrace widths, see for example a paper by Park and Huston of Sandia Laboratories in Surface Science. Also the degree of amorphousness of the surface can be measured by a number of techniques. In particular, one developed by Merill in Berkeley using helium atom scattering. In scattering helium atoms from the surface, the angular distribution of the scattered helium atoms is very sensitive to surface roughness, atomic roughness. So, I think we can determine these two properties. The surfaces we used are extremely uniform. The electron beam is about a millimeter in diameter and can be moved all along the surface. To that resolution, the surface is very uniform. But, again, diffraction discriminates against disorder.

Dr. McCormack: Whether we are looking at base metal versus noble metal or the selection of a transition metal sulfide on a support for HDS or whatever, we are prone as chemists to take our chemicals out of the bottles, make compounds in a standard way, put them in a reactor and see what happens. But clearly we don't know which crystal faces we are using. We don't know what promoters are doing to conduction bands. I would wonder, for example, in coal, where iron is an important element, which kind of iron are we using, which valence states, what states are on the surfaces. It's been bothering us for decades, I find no place to get good answers. Your techniques may be able to do it.

Somorjai: Well, it's clearly do-able and I suggest, buy an Auger spectrometer and measure what's on the surface.

McCormack: I doubt that you will find more than a couple all through the country in industrial laboratories.

Somorjai: Yes, but I think it is a communication problem and I am sure that it is changing.

Voice: I'd like to correct the price tag - it's closer to $25,000.

Somorjai: Well, we build our own and it is $5,000 if you build it at home.

Voice: You have suggested that the various catalytic reactions depend on the crystal orientation, is that true?

Somorjai: It depends on the reaction. The cyclopropane ring opening doesn't, but n-heptane dehydrocyclization, yes.

<u>Voice</u>: I was quite interested in the way the experiment is conducted. How are you able to determine the specific orientation of the crystal.

<u>Somorjai</u>: Look at the surface of a crystal with a back-reflection Laue camera to determine which face is the (111) face. Then you know it's face centered cubic; you look at the crystal zones and you cut it at 6.5 degrees to get a Miller index of 7,7,5.

<u>Voice</u>: You cut it in a vacuum?

<u>Somorjai:</u> No, no. These are stable; if they were not obviously we wouldn't be able to prepare them. Cutting introduces a micron thick layer of amorphous platinum because of the spark cutting technique used. Then you polish it and etch it in aqua-regia, to get the high Miller index. Next put it in the low energy electron diffraction chamber, and ion-bombard, heat, whatever you want, it does not change.

<u>Voice</u>: The reason why I brought this up is that some of the Auger Leed work is done by fracturing in a vacuum. You are positive that you have removed all the disturbed layer caused by spark cutting.

<u>Somorjai:</u> Well, if not we probably wouldn't get a LEED pattern.

<u>Voice</u>: Some years ago in Virginia they grew spherical crystals.

<u>Somorjai</u>: In fact, Gwathney's work is a most interesting one which has not been followed up, I don't know why. But he certainly showed that on oxidation of copper.

<u>Voice</u>: Incidentally, there would be no problem in taking those copper crystals and plating them with platinum; you might possibly get some epitaxial orientation as a consequence.

<u>Somorjai</u>: Yes, in fact there are so many crystal faces that one takes forever to go through all of them. The only problem is that if you have many chemical reactions at once, how do you separate them?

J. Bett: Since your slides showed such tremendous selectivity between different step distributions for the reactions of heptane, how does one explain the relative reproducibility of data reported in the literature for various reactions on dispersed platinum catalyst prepared without any great precautions as to which faces are exposed.

Somorjai: I wish I could know the proprietary information. What I think is happening is that these thousands of organic molecules of different types get on a surface where they form their various carbon structures and predose the surface so that it is reproducible. This could easily be checked, by putting something else on the surface like Haensel suggested, put say n-heptane on and then put on all the thousands of organic molecules. You might have a higher toluene yield because forming those carbon structures will catalyze formation of these organic molecules. But I am unaware of any patent, or published study, that would indicate that this is an explanation. So if I am wrong, there must be some other explanation.

Haensel: Let's put it this way. From a proprietary standpoint, you are not wrong. How's that.

Somorjai: You are a great help.

Wise: Is the ordered carbon structure a characteristic of the reaction or of the product? Have you pre-adsorbed the product on to the Pt surface?

Somorjai: Now, in that case, for Pt [6(111) x (100)] surface both n-heptane and toluene give the same ordered carbon structure. Now that may not be accidental at all.

Wise: You recall the work that came out of our laboratory on palladium where we found a template effect associated with isomerization of butanes. Is that unique?

Somorjai: That's why we are looking at gold. Maybe platinum is unique in forming these structures. But if that is the case, then the neighbors in the periodic table would probably do something very different.

Boudart: About anisotropy of reactivity and the comment that was made concerning Gwathney's work, I would like to make the two following comments. One is that the chemical reaction of the surface is not catalysis. The other remark is that Gwathney's work has been followed up by the people doing field emission and field ion spectroscopy where the same observations can be made much more conveniently.

Somorjai: On copper?

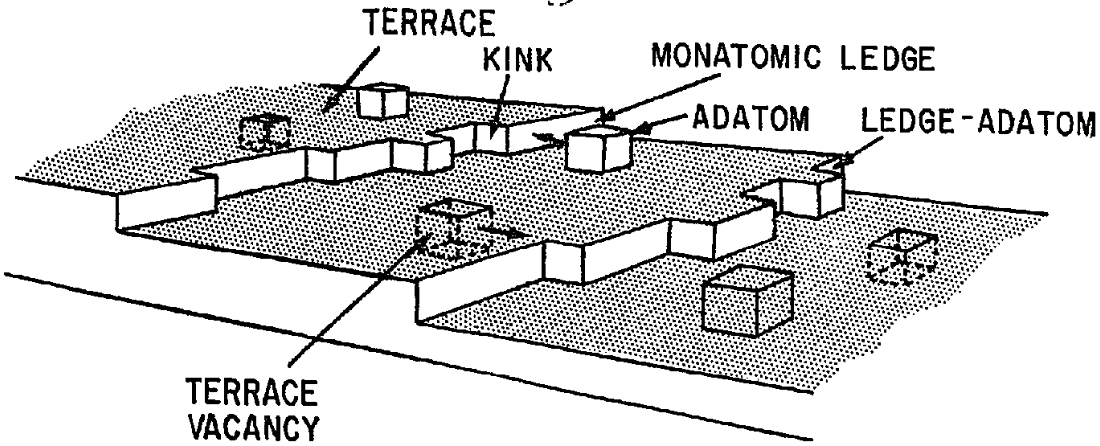
Boudart: I don't say copper, on some other material.

L. Libby: I would like to ask the academicians here if they would give us an estimate of the level of dollar funding of university research in catalysis.

Somorjai: Very low, whatever it is.

p

230



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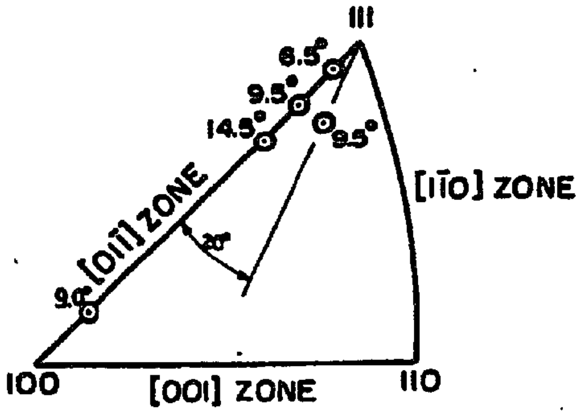
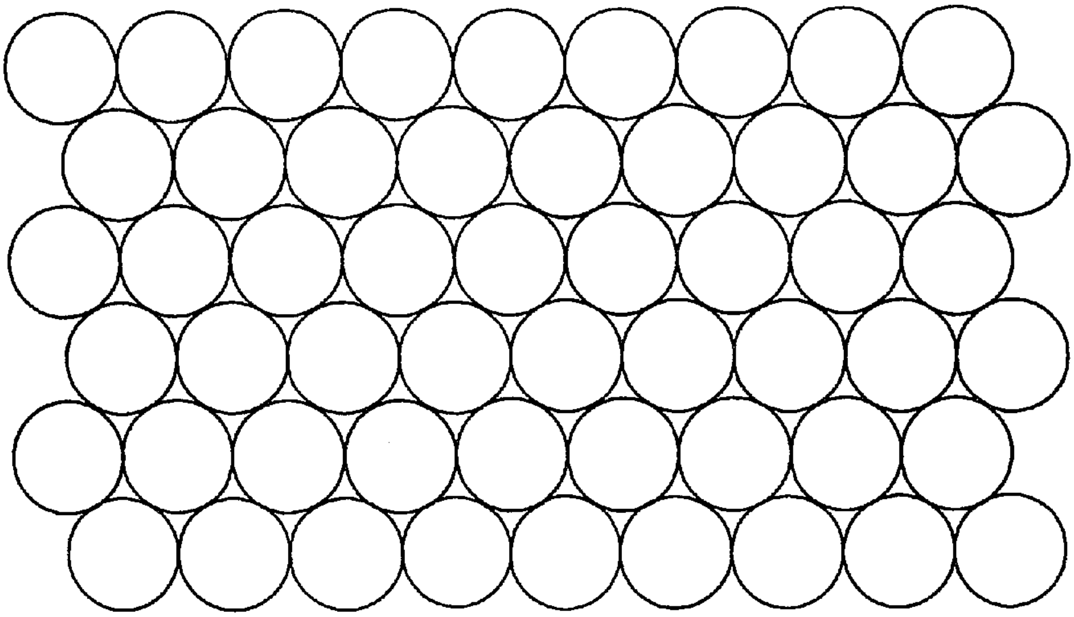


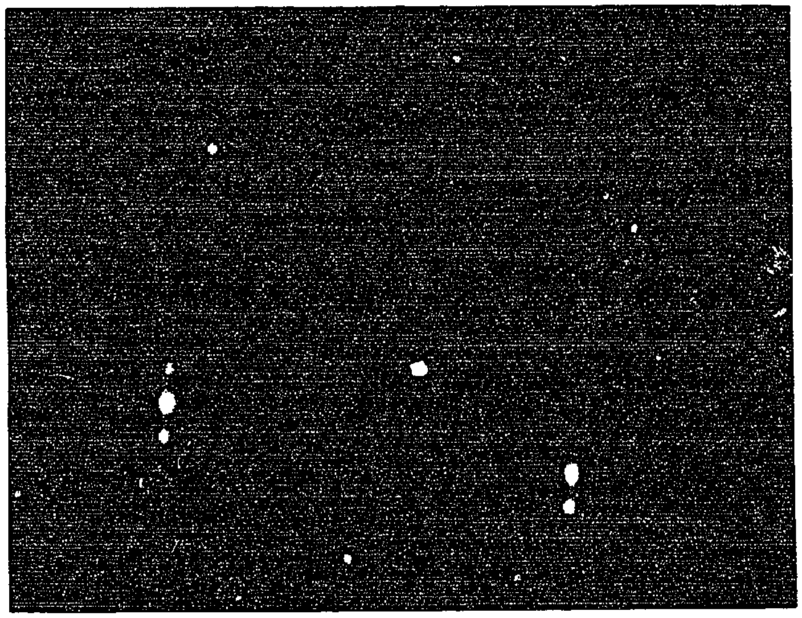
Table 1. Angles of cut, Miller index, and designation of the stepped surfaces of platinum.

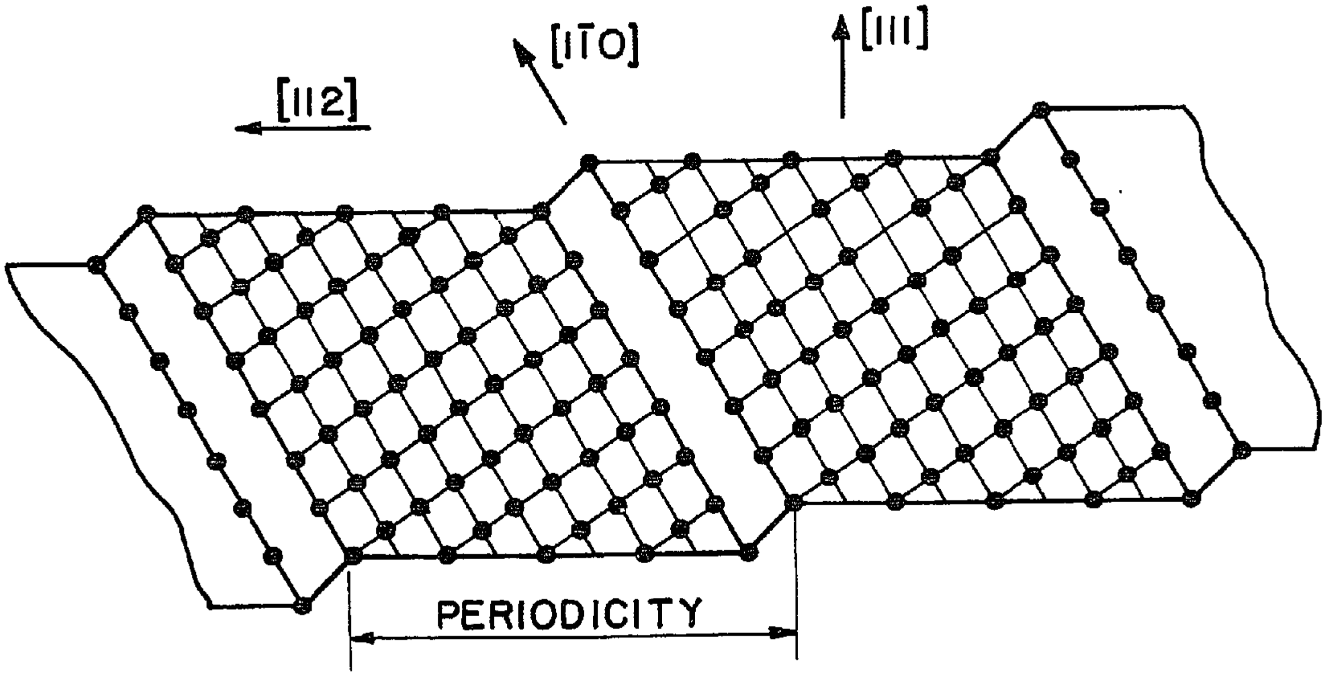
Angle of Cut	Miller Index	Designation
14.5° from (111)	(533)	Pt(S)-9(111)x(100)
9.5° from (111)	(755)	Pt(S)-6(111)x(100)
6.2° from (111)	(544)	Pt(S)-4(111)x(100)
9.5° from (111) rotated 20°	(976)	Pt(S)-7(111)x(310)
9.0° from (100)	(911)	Pt(S)-5(100)x(111)

p



Pt(S)-[9(111)X(100)]





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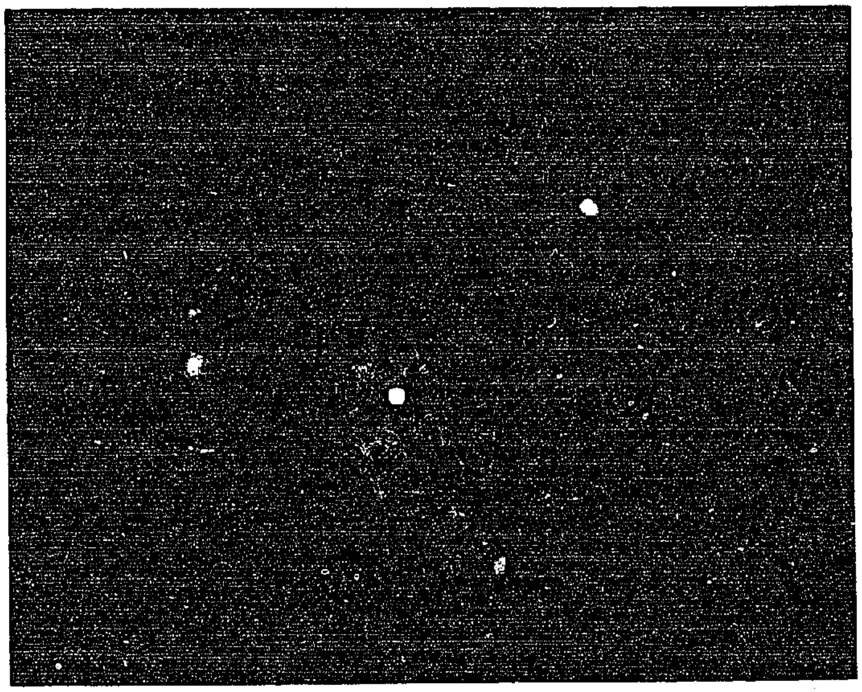
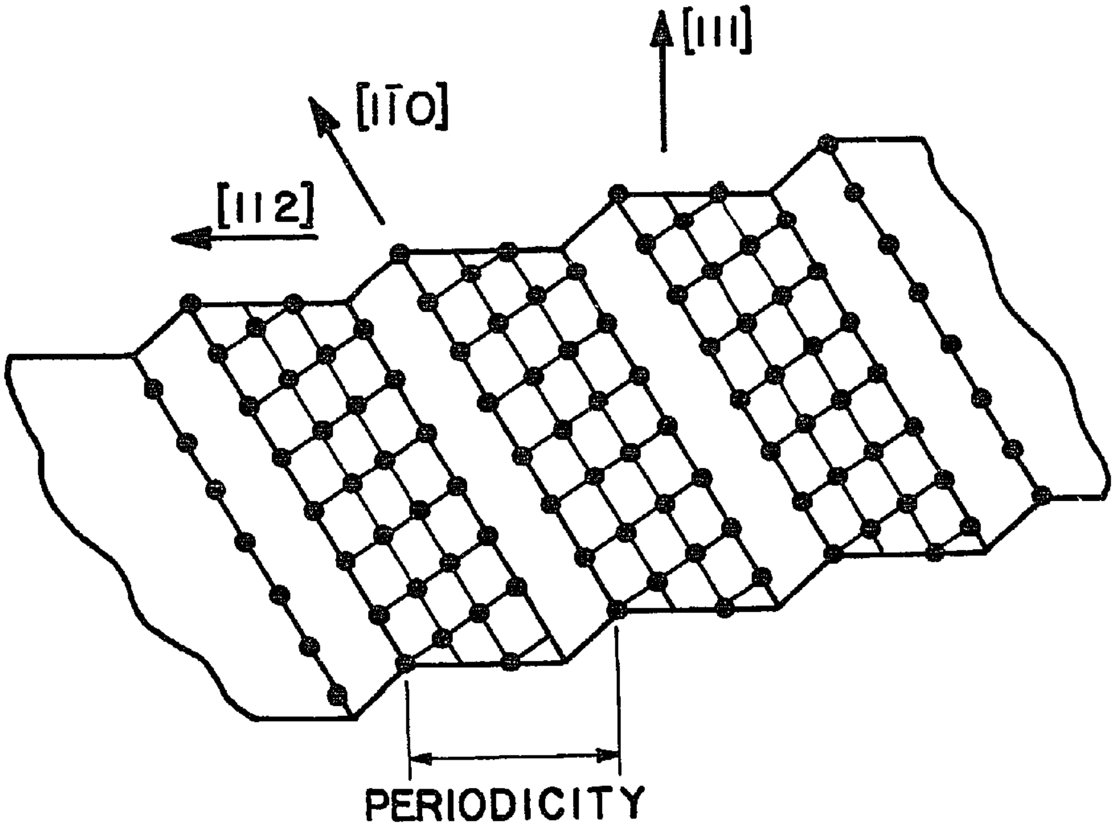
Pt(S)-[4(111)X(100)]





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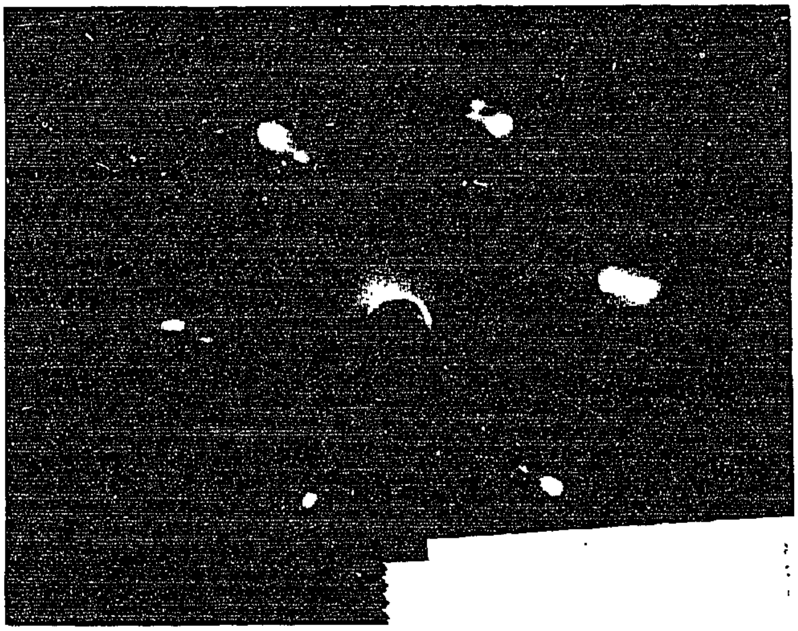
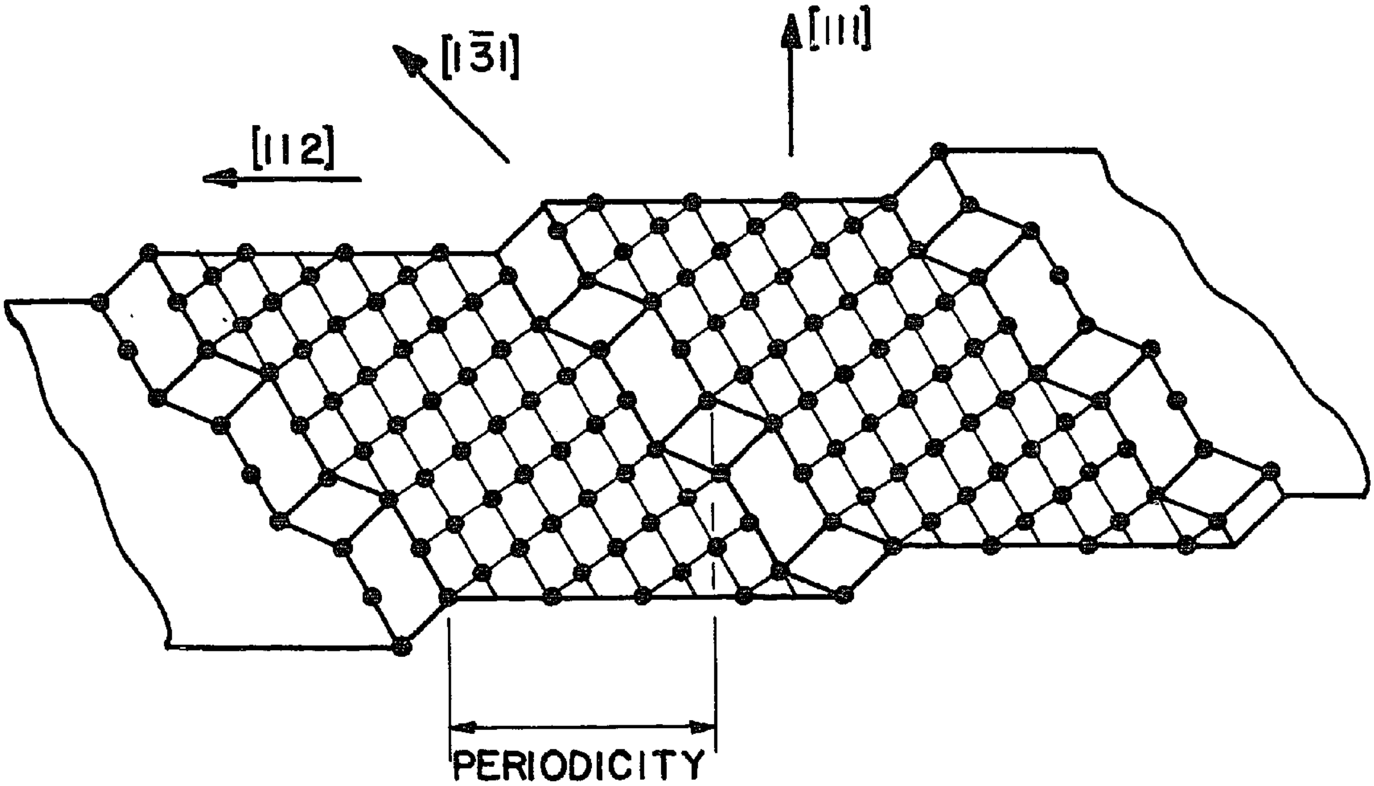
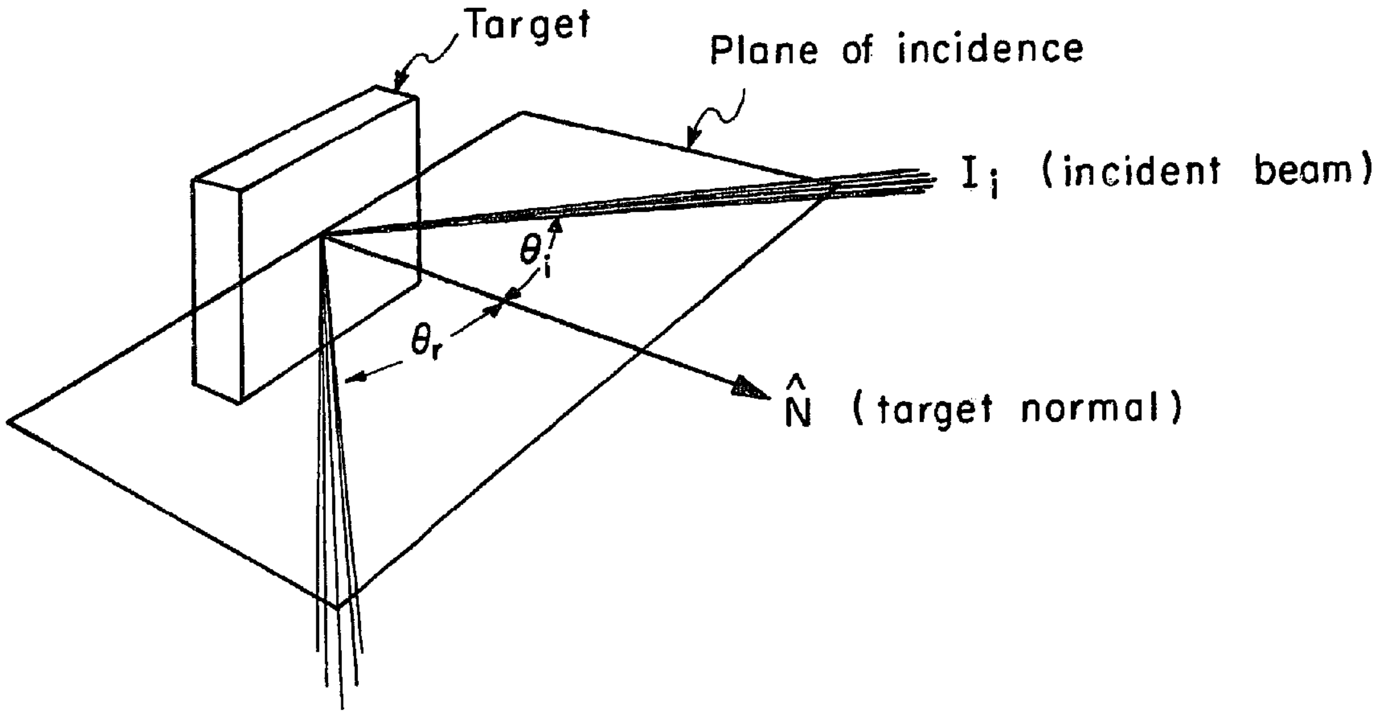
Pt(S)-[7(111)X(310)]







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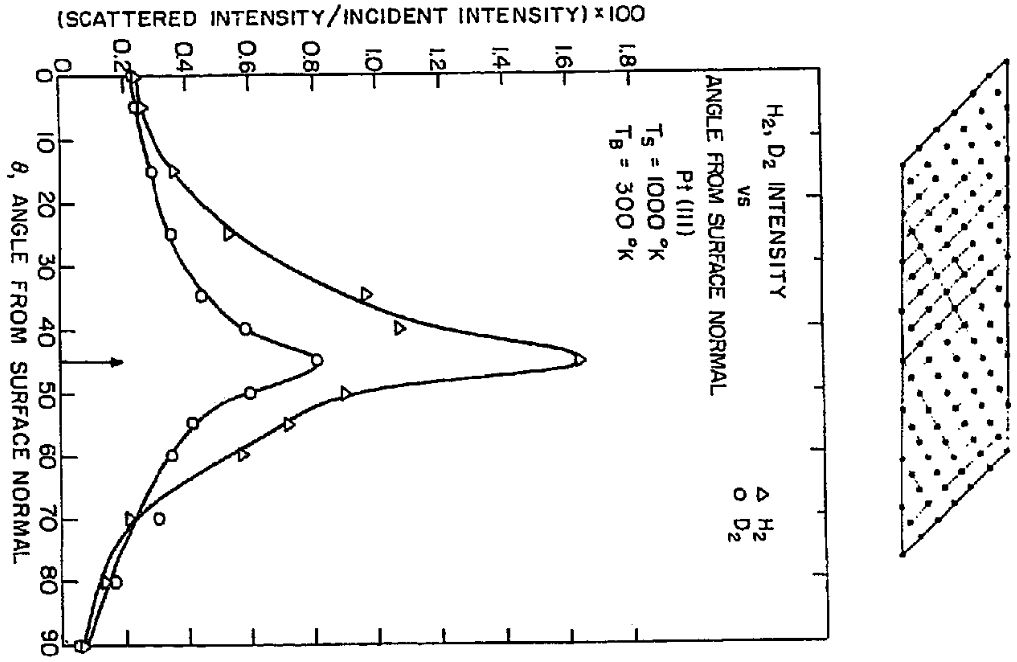
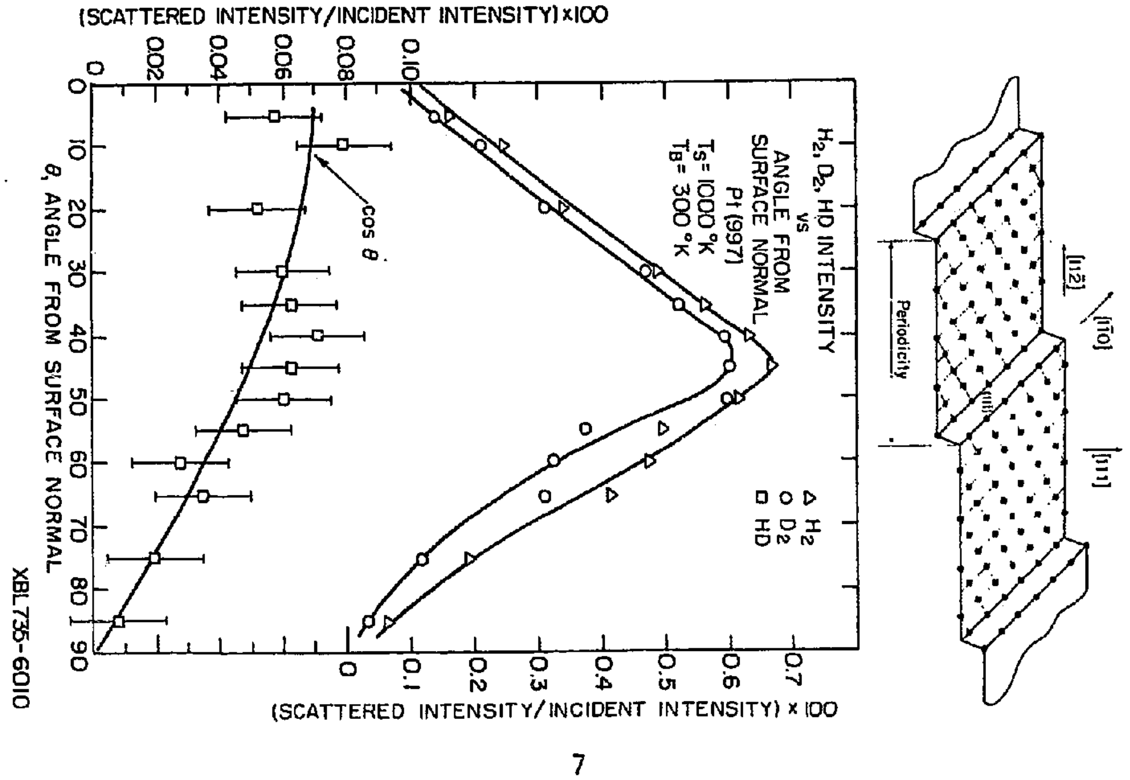


H$_2$, D$_2$ INTENSITY
vs
ANGLE FROM SURFACE NORMAL
Pt (111)
T$_S$ = 1000 °K
T$_B$ = 300 °K
△ H$_2$
○ D$_2$
[111]
(SCATTERED INTENSITY/INCIDENT INTENSITY) x 100
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
θ, ANGLE FROM SURFACE NORMAL
0
10
20
30
40
50
60
70
80
90



H$_2$, D$_2$, HD INTENSITY
vs
ANGLE FROM
SURFACE NORMAL
Pt (997)
T$_S$ = 1000 °K
T$_B$ = 300 °K
△ H$_2$
○ D$_2$
□ HD
cos θ
[11$\bar{2}$]
[1$\bar{1}$0]
[111]
Periodicity
(SCATTERED INTENSITY/INCIDENT INTENSITY) x 100
0
0.02
0.04
0.06
0.08
0.10
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
θ, ANGLE FROM SURFACE NORMAL
0
10
20
30
40
50
60
70
80
90

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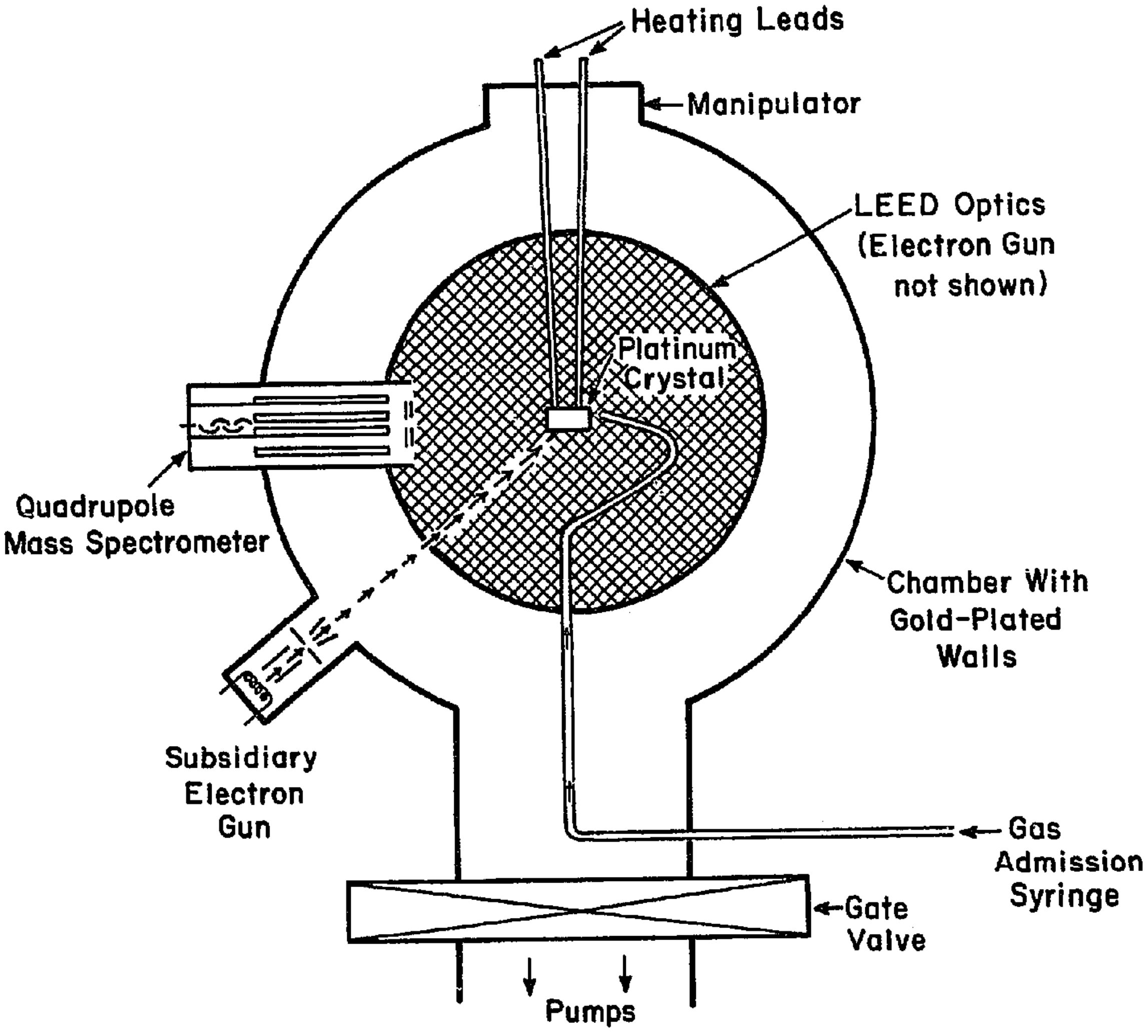
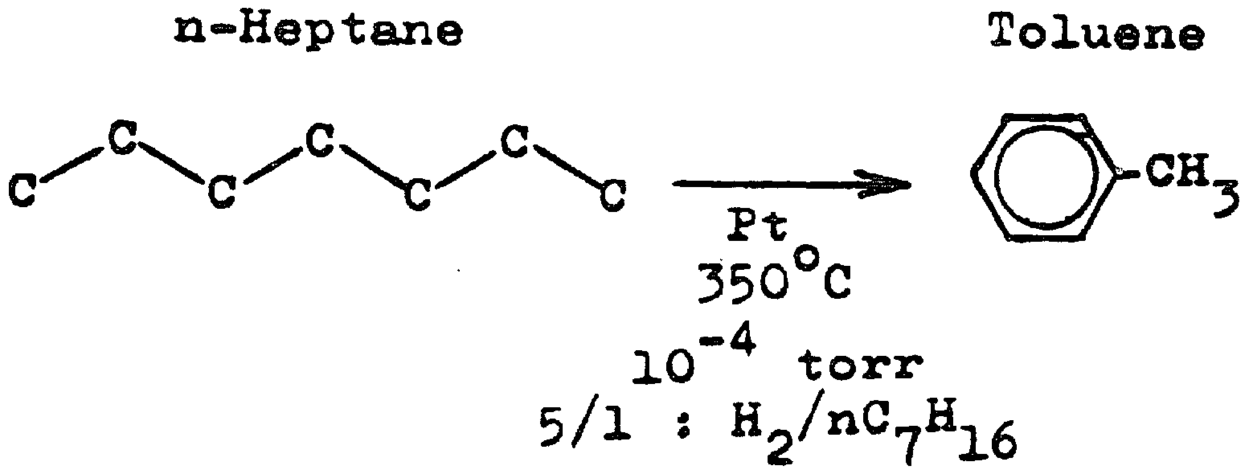
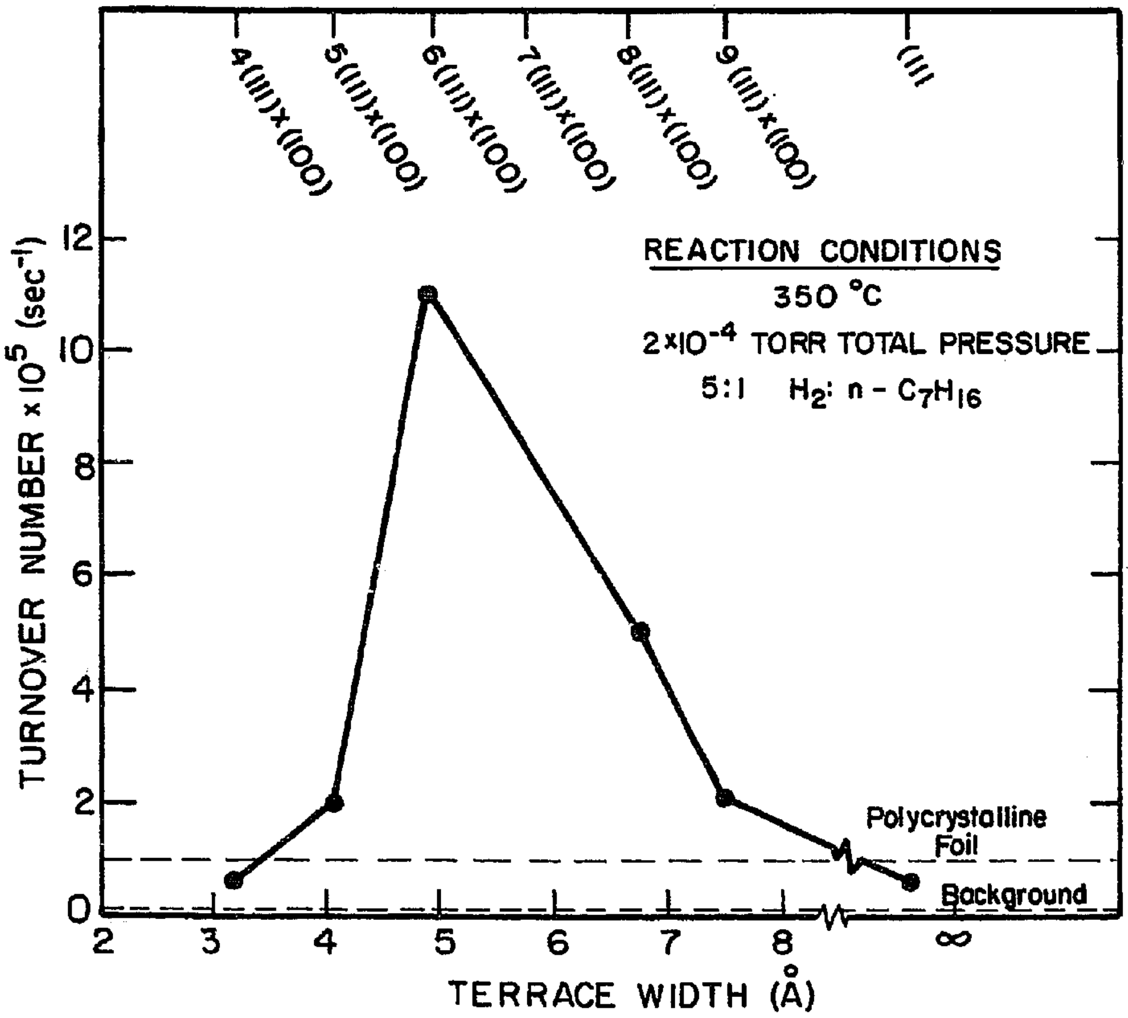

Heating Leads
Manipulator
LEED Optics (Electron Gun not shown)
Platinum Crystal
Quadrupole Mass Spectrometer
Chamber With Gold-Plated Walls
Subsidiary Electron Gun
Gas Admission Syringe
Gate Valve
Pumps

XBL 719-7296



DEHYDROCYCLIZATION OF n-HEPTANE TO TOLUENE ON PLATINUM STEPPED SURFACES



9

XBL739-1906

DEHYDROGENATION	Pt(S) - 9(111) X (100)
DECOMPOSITION	7(111) X (310)
NUCLEATION AND GROWTH	6(111) X (100) 5(100) X (111)
REARRANGEMENT OF SUBSTRATE	4(111) X (100)

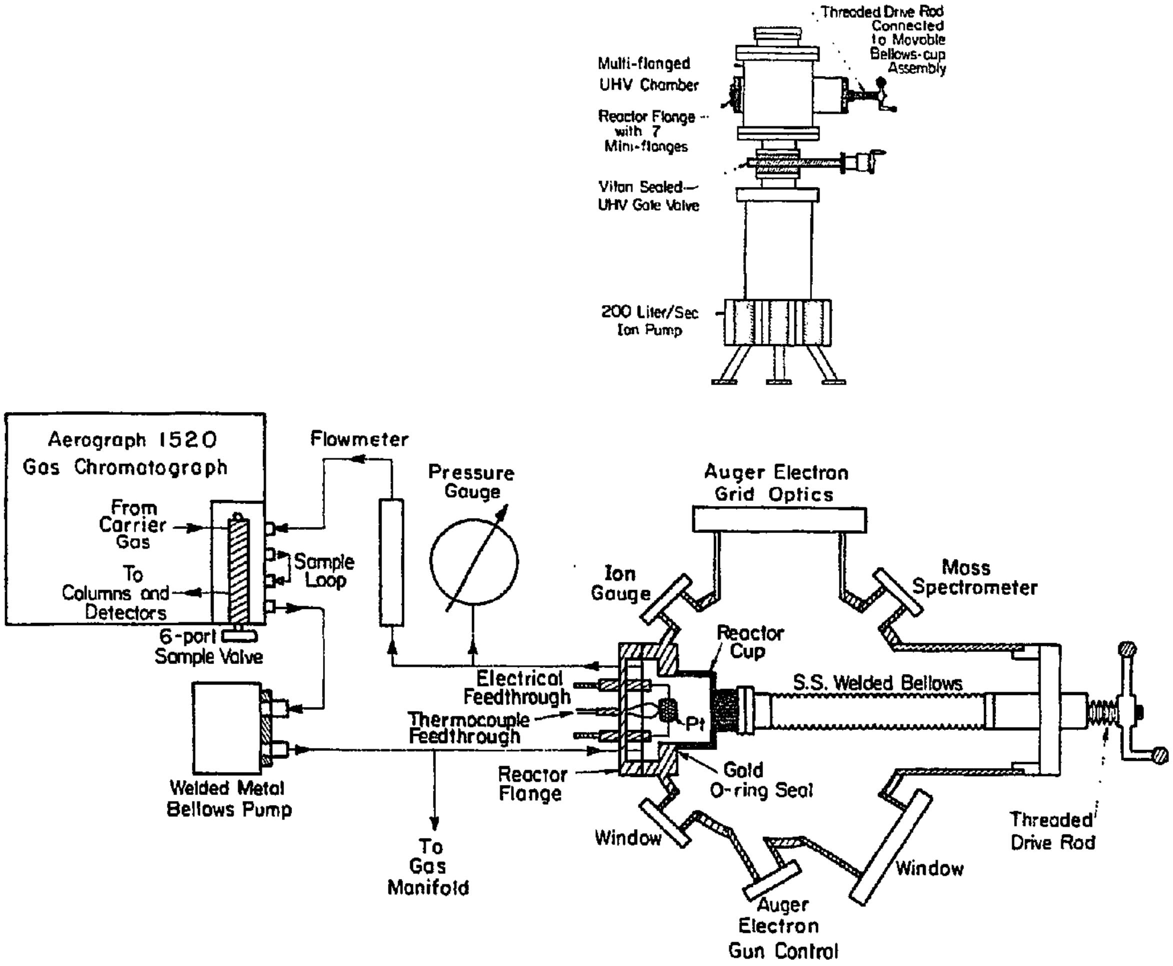
GENERAL MECHANISM FOR DEHYDROCYCLIZATION

Carbon Overlayer Formation

$$n\text{-}C_7H_{16} + Pt \xrightarrow[\text{STEPS}]{} \overset{*}{C}\text{-structure} + H_2$$

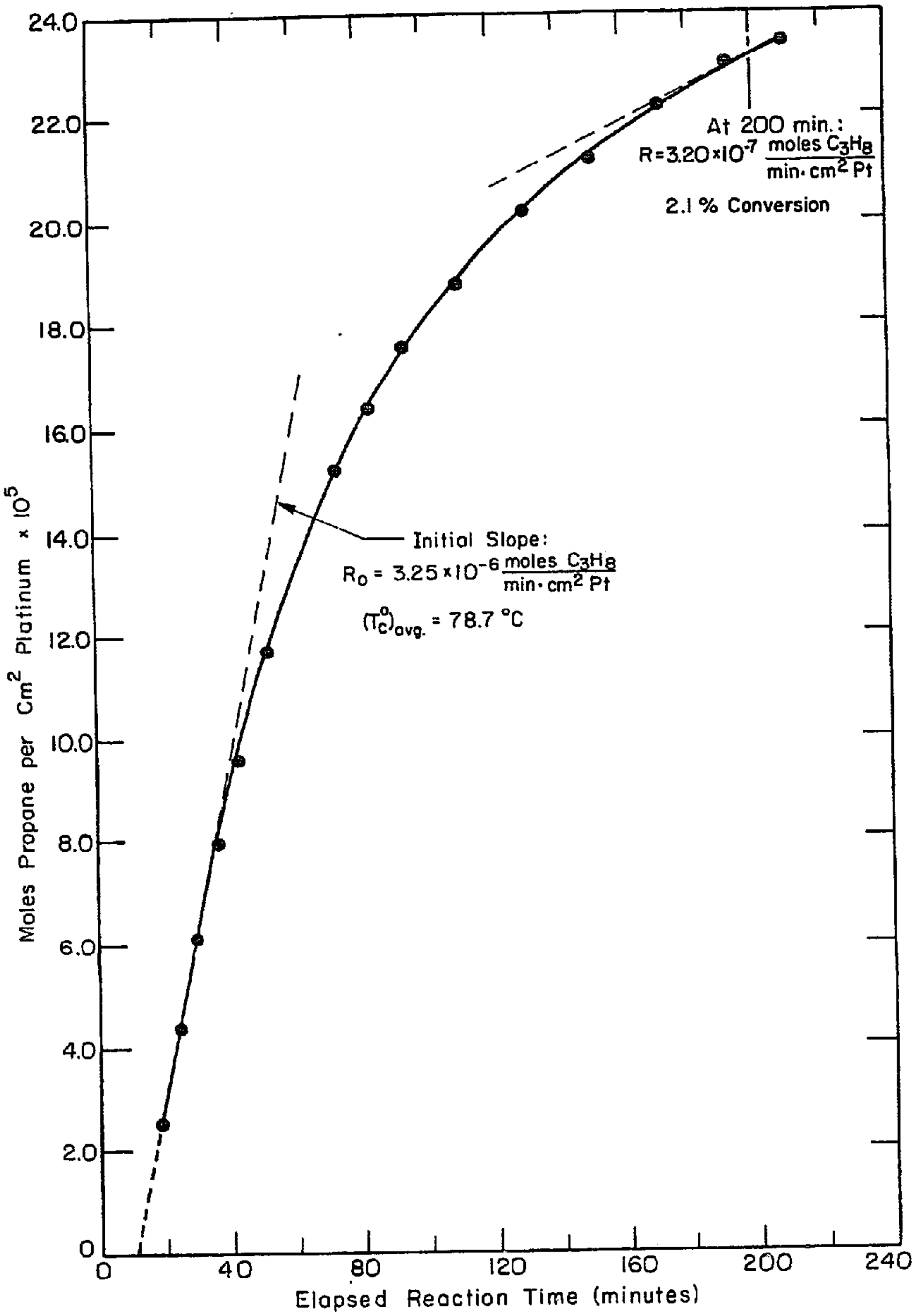
Catalytic Reaction

$$n\text{-}C_7H_{16(g)} + \overset{*}{C}\text{-structure} \longrightarrow C_6H_5\text{-}CH_3 + H_2 + \overset{*}{C}\text{-structure}$$

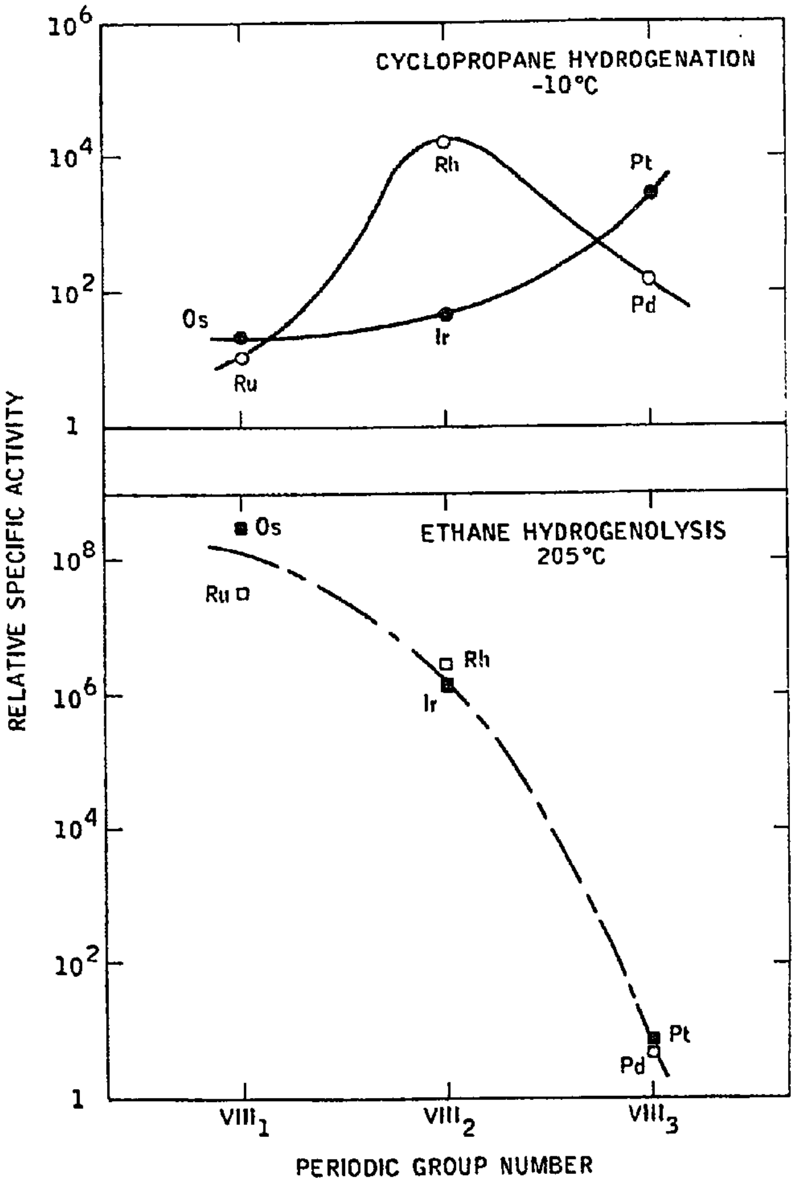


11

XBL 734-5969A


At 200 min.:
$R = 3.20 \times 10^{-7} \frac{\text{moles } C_3H_8}{\text{min} \cdot \text{cm}^2 \text{ Pt}}$
2.1 % Conversion
Initial Slope:
$R_0 = 3.25 \times 10^{-6} \frac{\text{moles } C_3H_8}{\text{min} \cdot \text{cm}^2 \text{ Pt}}$
$(T_c^0)_{avg.} = 78.7\ °C$
Moles Propane per Cm^2 Platinum $\times 10^5$
24.0
22.0
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0
0
40
80
120
160
200
240
Elapsed Reaction Time (minutes)

XBL738-1646

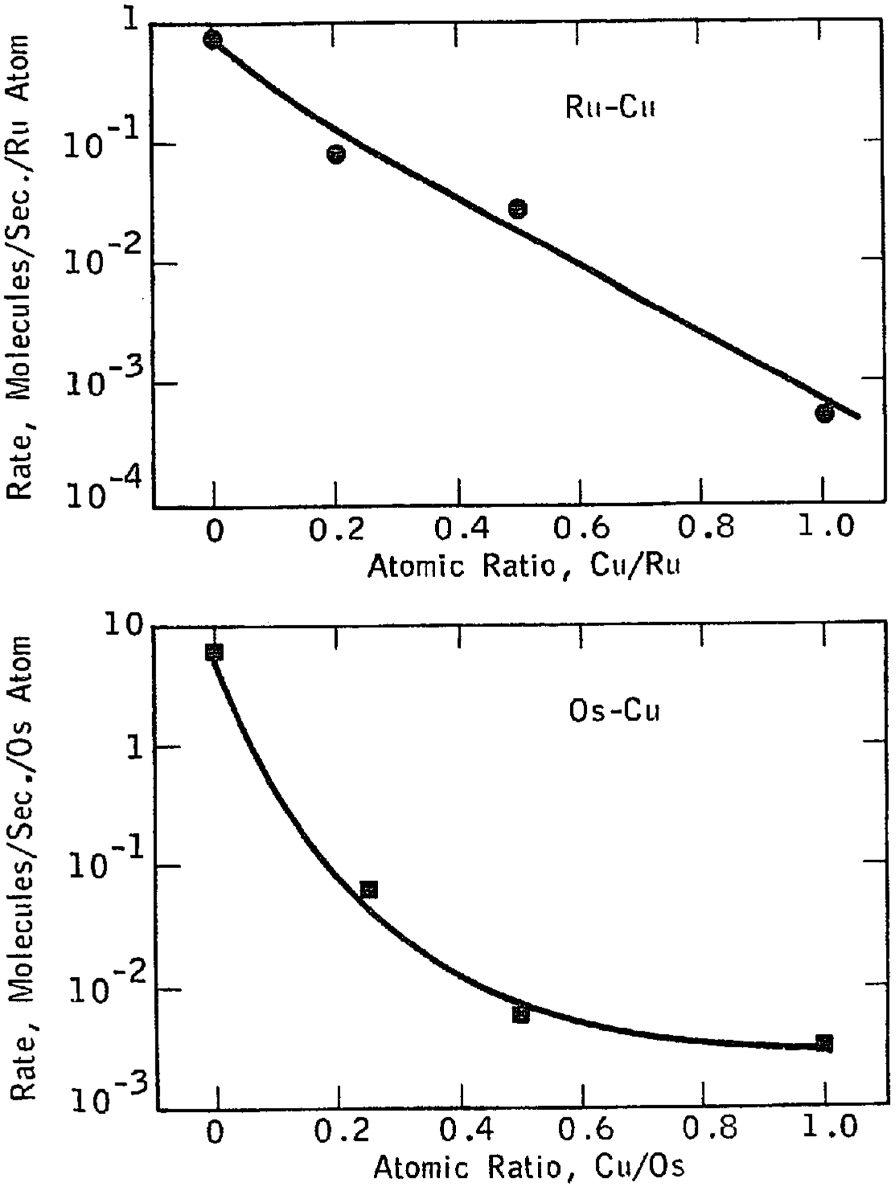

CYCLOPROPANE HYDROGENATION
-10°C
ETHANE HYDROGENOLYSIS
205°C
RELATIVE SPECIFIC ACTIVITY
10^6
10^4
10^2
1
10^8
10^6
10^4
10^2
1
Os
Ru
Rh
Ir
Pt
Pd
$VIII_1$
$VIII_2$
$VIII_3$
PERIODIC GROUP NUMBER

XBL 737-6503

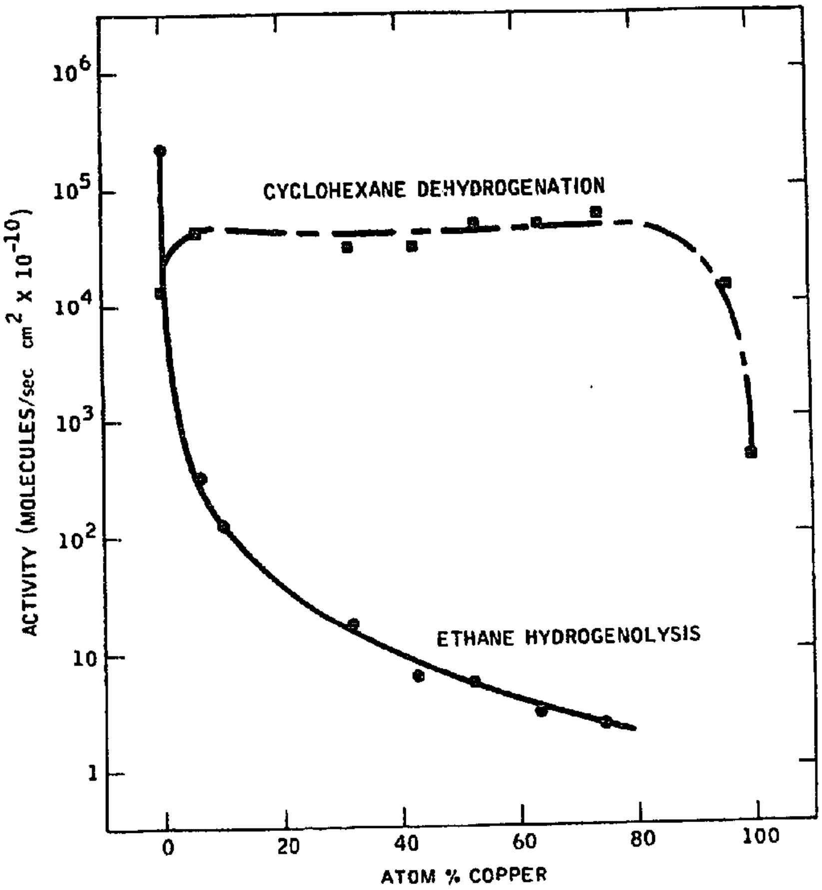
p

Comparison of initial specific rate data for the cyclopropane hydrogenolysis on platinum catalysts

Data source	Type of catalyst	Calculated specific reaction Rate @ P°_{CP} = 135 torr and T = 75°C		Comments
		$\left(\frac{\text{moles } C_3H_8}{\text{min} \cdot \text{cm}^2 \text{Pt}}\right)$	$\left(\frac{\text{molecules } C_3H_8}{\text{min} \cdot \text{Pt site}}\right)$	
Present study	Run 10A	2.1×10^{-6}		— Rate on Pt(s) - {6(111) × (100)} single crystal based on E^* = 12.2 kcal/mole.
	Run 12A	1.8×10^{-6}		
	Run 15	1.8×10^{-6}		
	Run 16	2.1×10^{-6}		
	Average	1.95×10^{-6}	*812	* Value based upon 87% (111) orientation and 13% polycrystalline orientation.
Hegedus[50, 51] See Table III-5	0.04 Wt% Pt on η - Al_2O_3	7.7×10^{-7} based on 100% Pt dispersion	*410	* Based upon avg. Pt site density of 1.12×10^{15} atoms/Pt site. This value would be nearly equal to average of above values if dispersion was approximately 50%.
Boudart et al.[23] and Dougharty[45]	0.3% and 2.0% Pt on η- Al_2O_3;	8.9×10^{-7}	480	— η_{CP} = 0.2, E^* = 8.5 kcal/mole.
	0.3% and 0.6% Pt on γ - Al_2O_3	2.5×10^{-6}	1340	— η_{CP} = 0.6, E^* = 8.5 kcal/mole. (Dougharty reports E^* = 8-9 kcal/mole and n = 0.2 to 0.6)

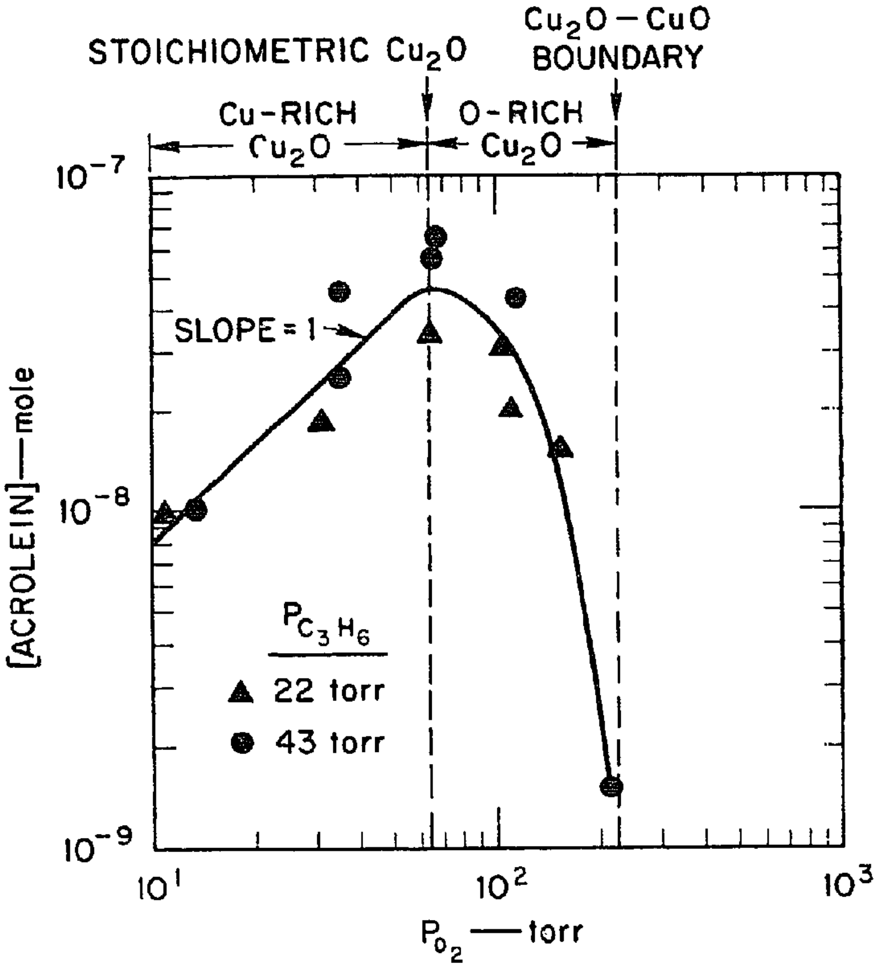

Rate, Molecules/Sec./Ru Atom
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
Ru-Cu
0
0.2
0.4
0.6
0.8
1.0
Atomic Ratio, Cu/Ru
Rate, Molecules/Sec./Os Atom
10
1
10^{-1}
10^{-2}
10^{-3}
Os-Cu
0
0.2
0.4
0.6
0.8
1.0
Atomic Ratio, Cu/Os

XBL 737-6500



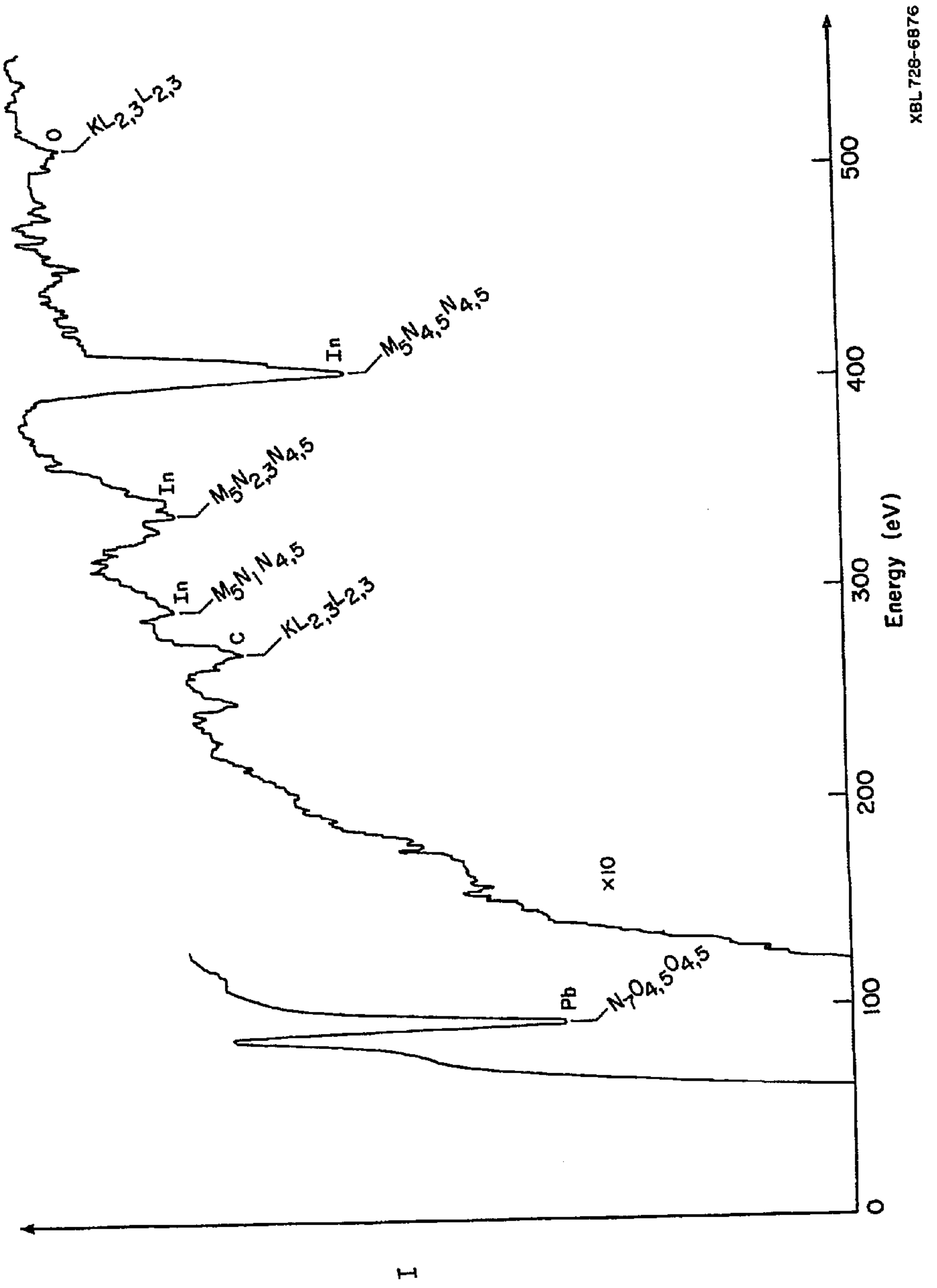
Activities of copper-nickel alloy catalysts for the hydrogenolysis of ethane to methane and the dehydrogenation of cyclohexane to benzene. The activities refer to reaction rates at 316° C. Ethane hydrogenolysis activities were obtained at ethane and hydrogen pressures of 0.030 and 0.20 atm., respectively. Cyclohexane dehydrogenation activities were obtained at cyclohexane and hydrogen pressures of 0.17 and 0.83 atm, respectively.

XBL 737-6506



XBL 737-6510

17


O
KL2,3L2,3
In
M5N4,5N4,5
In
M5N2,3N4,5
In
M5N1N4,5
C
KL2,3L2,3
Pb
N7O4,5O4,5
×10
I
0
100
200
300
400
500
Energy (eV)
XBL 728-6876

18

For an ideal solid solution:

$$\frac{x_2^s}{x_1^s} = \frac{x_2^b}{x_1^b} \exp\left[\frac{(\sigma_1 - \sigma_2)a}{RT}\right]$$

For a regular solid solution:

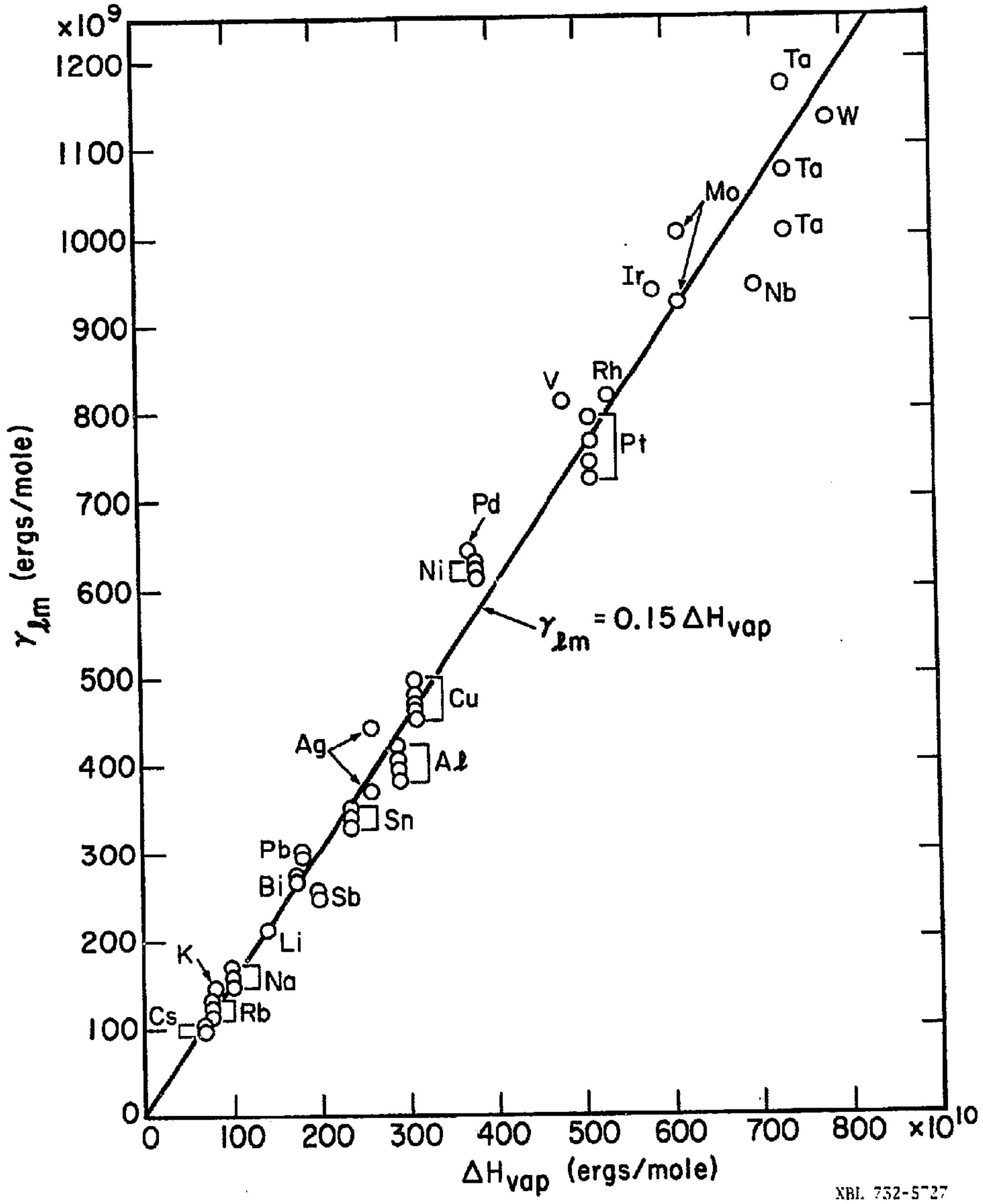
$$\frac{x_2^s}{x_1^s} = \frac{x_2^b}{x_1^b} \exp\left[\frac{(\sigma_1 - \sigma_2)a}{RT}\right] \exp\Bigg\{\frac{\Omega(\ell + m)}{RT} \Big[(x_1^b)^2 - (x_2^b)^2$$

$$\frac{\Omega\ell}{RT}\Big[(x_2^s)^2 - (x_1^s)^2\Big]\Bigg\}$$

where Ω = regular solution parameter = $\frac{\Delta H_{mixing}}{x_1^b \cdot x_2^b}$

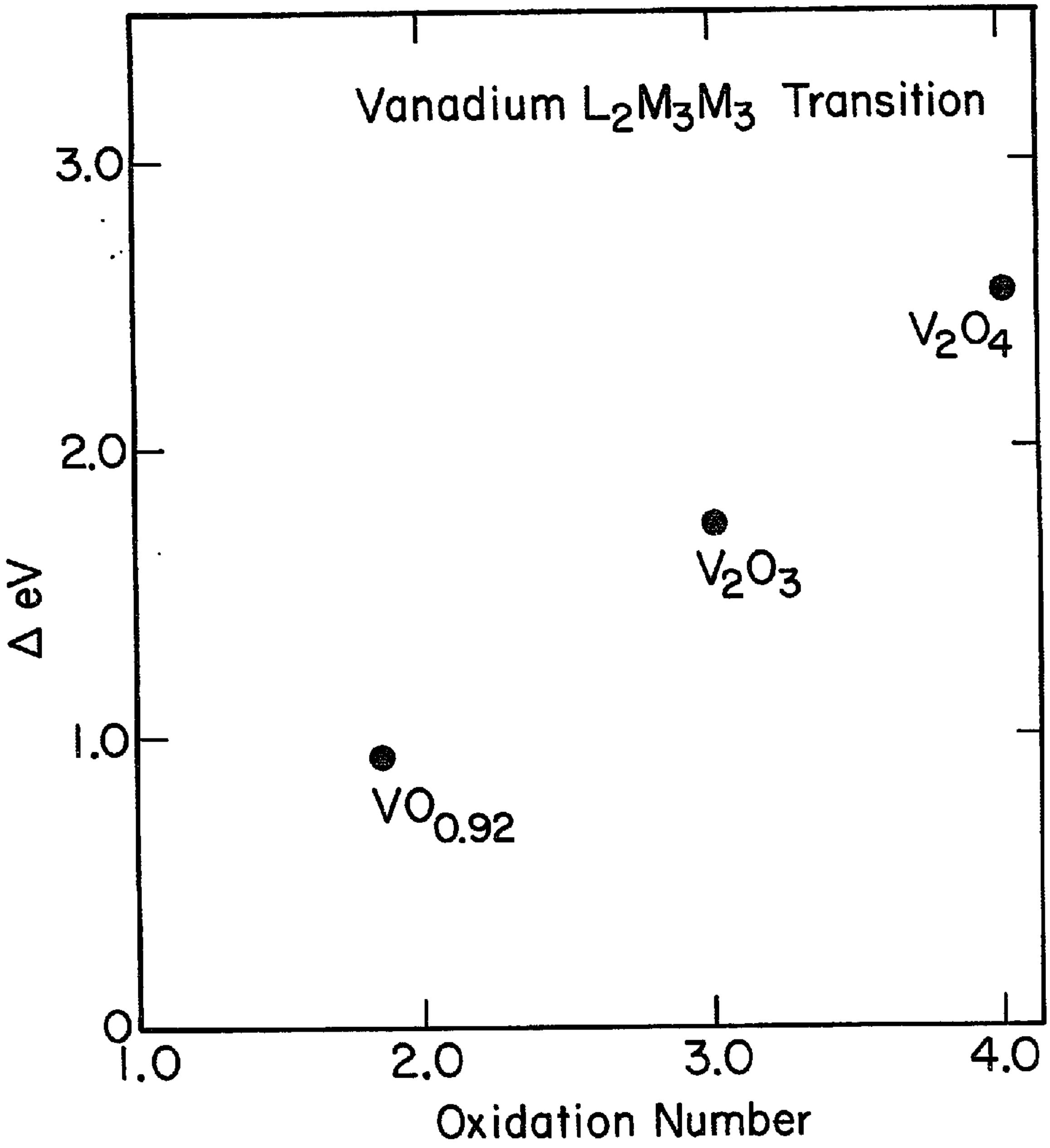
ℓ = fraction of nearest neighbors in surface laye

m = fraction of nearest neighbors in adjacent layer.



XBL 752-5727

20



XBL 7111-7645

(1) Catalyst particle structure can be reproduced on single crystal surfaces.

(2) Surface reactions can readily be studied on one face of a single crystal.

(3) Low pressure ($\leq 10^{-4}$ torr) and high pressure ($\sim 10^{3}$ torr) surface reaction studies can be correlated.

(4) Surface composition may be very different from the bulk composition for multicomponent systems.

XBL 7310-5478

INCREASING USE OF JET FUEL FOR PEAKING POWER

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Institute of Geophysics and
Planetary Physics
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I apologize to those of you who know this important matter; it's roughly as important as the loss of mileage due to smog control devices. The point is that the management of large utilities requires that a certain part of the generating capacity be rapidly switchable. In recent years everything has been done to increase the efficiency of the base load generators. The atomic power plants and the high powered, high temperature fossil fuel plants built in recent years are totally unswitchable so that about two thirds of the present day electric power is now essentially unswitchable. There are thermal stresses involved and besides, there's too much capital involved to turn them off. In the past the electric power industry has used the obsolete plants for peak power. But it takes several hours to turn on or off a thousand megawatt plant no matter whether it's coal fired or it's oil fired. So they can't be used for peaking. Instead jet fuel is used. So the outcome is a shortage of gasoline which roughly matches the catastrophic fuel shortage due to the reduction of compression ratio in the automobile plus the elimination of lead tetraethyl. There's no secrecy about this message, but it somehow hasn't gotten through to people yet. Things are bad and getting much worse. Here's what the power industry is doing. They're buying airplane engines and running them on airplane fuel. Southern

California Edison bought something over three million kilowatts in the last two years. Con Ed has done likewise but this means an increasing extra load on the refineries. I'm carrying the word to you tonight based on the work of Les (L.G.) Cook of ESSO Research and Engineering. The story is Les's and he's dead right. Our energy shortage is going to be much worse than we've seen it yet. The only way out of it that I can see is development of catalysis. We've got to pull the rabbits out of the hat; our situation is extremely dangerous.

I'm strongly in favor of an energy-environment agency like NASA. This is an international problem. We make tremendous decisions without considering the consequences like the public utilities deciding to buy jet engines for peak power. In most power plants the peaking required is 25% of the total power for rapid switching and the installed capacity must be about twice that. Now there are visionary plans and ephemeral thoughts about using batteries, and pumping water into high lakes, and various other ways of obtaining local peak powers. But fundamentally the energy shortage is much worse than is commonly known. I expect to see gasoline at a dollar a gallon shortly. I don't see any way out except to attack the problem with catalysis. That's the point of this conference. I hope tomorrow we'll have some talks about a Catalyst Institute. But, in the short term we've really got to get with it and pull some rabbits out of the hat. We fell into a trap. We thought that cheap atomic power and high efficiency fossil plants would insure the electric power demand. Nobody quite realized the problem of peaking. A little like the auto catalyst problem and the lead tetraethyl problem. First we reduced the compression ratio on the engine in order to cut down the problem of NOX, as a result of which we're losing mileage. And this buying of jet engines by the power companies is commensurate with the auto engine cut.

Emmett: How do catalysts come into this, Bill?

Libby: Well, if we had a good automobile catalyst we could keep the lead and keep the high compression ratio and that would save us about 28% on mileage. This problem could be solved with the proper catalyst.

On the matter of the peak power, what we have to do is develop a super conducting cable with which we could wheel power from very large distances, more than in a 600 mile grid so that we would not have to have available extra local peaking power on short notice. Strangely, the chemistry of catalysis and super conductors are very closely connected. We are at the crossroads of major technological decisions. Instead of going away, the energy problem is going to get worse and worse. The reason for this conference is so ARPA and the DOD can have the chance to help us do something about it. Now, take the auto catalyst problem, the first point of removing the lead is that it will poison the platinum catalyst. The first reason the compression ratio was reduced was so we wouldn't need a catalyst. This, plus making the cars heavier and with more air conditioning has caused close to 30% reduction in mileage in the 1974 model cars. We're facing a dollar a gallon for gasoline.

Haensel: I don't know that we are facing that at all.

p

Libby: We have 50 cents already, Val.

Haensel: Yes, but I don't see any reason for the dollar.

Beuther: We're facing the dollar some time, it may be 1980, I don't think it's going to be 1974 or 1975.

Libby: Well, Val, if you were buying a new car, would you buy a big Cadillac?

Haensel: No, I'm going to hold onto the car that I have with a higher compression ratio engine.

Libby: Next year we get about 20% of that gas mileage back when we put catalysts on the cars. No. There's no doubt about it.

Hightower: But you said a 34% reduction,

Libby: I said 28%.

Hightower: Is 28% relative to 1968 cars?

Libby: Relative to uncontrolled cars.

Haensel: Uncontrolled cars was not '68 but '71 and '72, and '73 isn't that right, Dick?

Klimisch: No, it was 1966.

Libby: Well, I drive a '66 Toronado and it makes 14 miles a gallon. I hate to tell you what the '74 Toronado does.

Emmett: Six miles a gallon.

Libby: That's right. We have a problem. My point tonight is to say not only the automobile but also utilities are going to make tremendous demands for increased use of jet fuel. That's Les Cook's message.

Haensel: Bill, I disagree very violently with you in some respects. I do not believe that economy and environmentalism are at odds. But you said, for example, let's go back to leaded fuels. I don't see any reason for it.

Libby: No, I said that's a possibility.

Haensel: Okay, because other countries are saying we don't like lead and EPA doesn't like lead for reasons other than the catalytic converters.

Libby: I am saying that there's an additional crisis you might not have realized.

Haensel: Oh, I appreciate the additional crisis, yes.

Libby: I'm sure you do, but there are some people here tonight who never heard that utilities are buying airplane engines to make electricity.

Haensel: We could resolve the crisis in a much better way if all the utilities would burn low sulfur coal and all of the transportation systems would use crude supplies and all of the home heating and cooking be done by gas. Right now in California, most of the utilities are run on gas which is an extremely valuable commodity.

Libby: We'd rather have all of them go on gas or atomic power rather than coal.

Haensel: What's wrong with coal burning? We have 300 years' supply of coal. Bill Bailey, are you with us?

Bailey: I'll argue with you on the dollar a gallon gasoline; I think you're altogether wrong, Val. I think it's coming in the next two or three years.

Haensel: All right. Don't you think it's worth while for the utilities to burn coal?

Bailey: This is exactly the thesis I was making.

Haensel: That's what I thought.

Bailey: There is technology which will allow the utilities to burn coal and that is, first, stack gas clean up and, also, synthetic fuel production. Technology can solve this problem to any degree set by a national energy policy. That is very difficult since there is no national energy policy.

Libby: That's the seat of our difficulty. We have no energy policy. Most of the guys making the decisions on energy policy are not very skilled.

Heansel: But,although catalysis is nice work, I cannot see direct application of catalysis at this point. In what way do you see it?

Bailey: For the optimum conversion of fossil raw materials other than petroleum to fill our energy needs while maintaining some environmental conservation starting by burning low sulfur coal to fill the gap. Then we have to tackle the problem of using coal in order to meet the need of the liquid fuels and methanation to form pipe line gas.

Haensel: Right, I think we're only arguing about a time basis.

Libby: Con Edison in New York has a one-month fuel supply if they are well off. And they're lucky to have one month. And now they have been cut off of low sulfur oil and they have no choice but to go to the governor for a variance saying you must give us a hearing.

McCormack: To my knowledge, we do not have coal capacity in the country now to take care of more than a very small fraction of our utility needs. Many mines have shut down because of increased operating costs and it takes roughly two to three years to replace utility gas and oil by coal.

Voice: A lot of electricity is made by coal today.

McCormack: Half of it is now but the other half is what you have to produce to return to coal. We need about 300 million tons per year now and we don't have the capacity for another 50million tons per year production, as I understand it. It takes about three years to open a new mine.

Voice: Not so long for strip mining. Another point is that coal mines run five days a week, eight hours a day. If you want to mine more coal it's possible to lay on more shifts so thereis flexibility to increase production maybe 20%. Now beyond that then you're right basically.

McCormack: That's about 50 million tons per year.

Voice: There's another problem with the utilities, though. Practically all the utilities on the east coast have equipped their docks for loading coal, the rail facility areas for storing coal, and now they are all equipped with storage tanks for oil. It would be a very difficult operation to re-convert to coal.

Libby: Now, we're facing a situation where there may be a kind of move to scrap the environment quality control programs. We need not let this go that far. We must create a national energy policy which is sensible. I couldn't help but think today when we heard the paper on the oil shale about the supply of water on the shale lands and how short it is. When it comes to dealing with energy matters, we forget to take the whole broad picture. I was on the state Air Resources Board when we decided to reduce the compression ratios in the engines.

Hansel: You didn't decide that. Detroit decided that. Isn't that right, Dick?

Klimisch: We don't remember those pressures.

Libby: Well, you had to meet emission standards, which were set by the state.

Klimisch: No, we had to make it possible to use catalysts in cars. The only way to do that is to remove lead from the gas.

Libby: With present technology you're probably right. But I think it's possible with future researches to tolerate lead.

Haensel: Is it? I don't think so.

Libby: I said future research, Val, you can't possible refute the possibilities of future research.

Bailey: You can say it's highly unlikely, but not impossible.

Haensel: Bill, if you go to higher compression ratio engines, you will need 8% less crude to drive the same number of miles. I think we must consider the total picture. We should drive smaller cars, but we have a hundred million big cars on the road right now that have to be driven. So we're sort of stuck. We can only work with the incrementals. And even if the incrementals are subcompacts, they're not going to be a large percentage of the total.

Klimisch: I think they're not going to be a large percentage of the total. People don't want them.

Burwell: They can be made to want them.

Bailey: No, sir. We argued about that at breakfast and I'll argue with you again. In Europe, taxation is enormously high, gasoline is over a dollar a gallon, more and more cars are going on the road in Europe and they are bigger and bigger cars. Taxation does not stop it.

Voice: Well, Bill, when I go to Europe my immediate reaction is My God, they're all driving around in Kiddie cars. Then I come back to the United States and I think everybody is driving around in a Mack truck. I agree that this is a European view point that more people think they can drive around in a Peugeut 504 than a Citroen 12, but this is all relative. The existence of one dollar a gallon gas is going to make a lot of people go to smaller cars. Although it's true, if you care enough you'll still buy a Cadilliac.

Libby: But, Bob, don't you think that we'll come to the time when society will frown on a person who drives a Cadillac?

Voice: If I've gone without gasoline for a couple of weeks, then I may look upon a Cadillac driver as a public enemy.

Klimisch: I don't think you understand quite how people buy cars. We've been trying to understand that for years. We recognize the great savings that small cars represent. We'd like to make small cars. We really don't know how to do that and still stay in business, but we're looking very hard at that.

Haensel: What are you doing, Dick, about making cars that are just as large as ever but are lighter weight? Is there any work being done on that?

Klimisch: Yes, every year more of the metal is replaced by plastic . . .

[illegible] I think that it is true that people have bought what they want, but I have not seen much advertising from Detroit that leads me to want a small car and it seems to me I've seen advertising designed to make me want a big car, but perhaps I've misinterpreted it, it's been the other way around.

Klimisch: No, no. That's not true. We don't know how to make money making small cars.

[illegible] That's fair enough. I'd say basically that you've made cars you can sell, and that's all that anybody else does. But I still have confidence that the economic animal is influenced by money and that a suitable taxation policy can make a change.

Libby: But, that can only be done if people agree, and they don't agree. For example, EPA comes into Los Angeles or New York City and says, you've got to charge your employees $2 a day for parking if they come one person in a car; if they have three persons per car it's free. As I assess it, this won't work.

[illegible] Well, I quite agree that example won't work, but when your prediction which I think you're right on, if $1 per gallon gasoline comes true then I think people's opinion will change. At the moment, very few people understand the situation. I talk to people who say, "Look, why don't you chemists go out and get other kinds of energy?"

Libby: Good question.

Beuther: If you're smart, there must be other kinds of energy to get. But I think after things have gotten tough enough, opinions will change.

McCormack: In some respects, the taxation policy is working. The taxation policy of the Arabs, Venezuelans, and the Canadians is providing quite an incentive. . . That was the Big Deal.

Voice: That was a good statement.

Libby: Well, we don't want to prolong the meeting, I did want to say to you that this peaking power requirement where the Utilities are buying airplane engines is a major matter, an additional load on the refining industry which we don't need.

Haensel: Bill, what difference does it make as far as what's coming out of the front end of a refinery. It costs the same for me or you whether it's naphtha, low sulfur resid, gasoline or propane, so what difference if a Utility is buying naphtha to run a turbine?

Libby: Instead, the Utilities could run the power plants on coal or nuclear at peak power all the time and store the off-peak excess by producing hydrogen for example. Then there would be no extra load on the refineries.

Voice: Also, if you can desulfurize coal you will relieve the petroleum industry.

Libby: Look, there's nobody in this room argues about "we have to go to coal," nobody. The question is how can we do it with the least insult to the environment.

Voice: It certainly makes a great more sense to turn coal into SNG and pipe it, than it does to have trains carrying coal from west to east.

Libby: There is a Louisiana power plant being built close to Baton Rouge which will run on Wyoming coal. Eleven hundred megawatts on coal carried from 1100 miles away.

Haensel: Bill, it's something like this. A lady in Boston turns on her electric range to boil a pot of tea and this requires an Arab to turn on an oil pipe in Arabia, filling tanks that are shipped half way across the world, into Houston, and somebody else distills the product and converts the naphtha to SNG. SNG is piped out to the electrical utility in Boston, the utility in Boston burns it to make electric power so the little lady can have her tea. Can you imagine the efficiency of each step. I mean its's ridiculous.

Libby: But, my complaint is Baton Rouge adjoins the richest oil and gas fields in the world and yet its electric power will depend on hauling Wyoming coal. There's something wrong with that policy.

Bailey: But, even in the richest oil fields in the country, a refinery may not be able to get guaranteed natural gas to burn in its furnaces. We're that short.

Voice: You're that short in Houston?

Bailey: Yes, but I was speaking of Louisiana, where they're richer in natural gas at the moment.

Voice: But the city of Houston can't even get liquid fuels for its future electrical requirements and it is putting a nuclear reactor in Bay City.

Bailey: They're doing that because of the price crunch more than anything else. Natural gas has been artificially priced for so long that we're running out. We've wasted a tremendous resource by under pricing by law.

Libby: We're obviously going to have to struggle for some national energy talks. My constant concern is to get some catalyst input before the present technology is frozen.

Haensel: I'm afraid they're putting freezes on present technology because the catalytic technology at this point is not ready as far as coal conversion is concerned.

Mills: Coal gasification may be a well developed technology by 1978, 1979, but at present all we have is the German technology of 1945.

Haensel: Some 17 million barrels per day is the crude equivalent that we need now?

Libby: Yes.

Haensel: And even if Alaska opens up in 5 years, it will provide only about 2 to 3 million barrels. That's small.

Bailey: North Slope Alaska. If we used only that, it would last not more than three to four years.

Fisher: Are oil wells pumping in capacity now?

Libby: Well, it's a tertiary treatment challenge. A main hope is improvement in this area.

Fisher: Are catalytic techniques being used in recovery stimulation?

Libby: No, now it's mainly a matter of water. Except in this very indirect way, George. The desulfurization of stack gases produces enormous amounts of sulfur which could be put into sulfuric acid. It's conceivable that this could be beneficial in the tertiary treatment process because of the limestone content in most formations. Most oil producers are thinking of $3.00 a barrel, but when they get used to $7.00 a barrel, they may think a little differently about the cost of tertiary treatment with sulfuric acid. I think a lot of things in this general pattern of synergistic effects may become important and one area where we are doing something really substantial is the area of catalysis.

Hightower: Bill, thank you very much.

(The report of L. G. Cook, Corporate Research Staff, ESSO Research and Engineering Company, May 1973, follows in abbreviated form.)

THE RAPIDLY CHANGING TECHNOLOGY OF ELECTRICITY GENERATION AND MAJOR CONSEQUENCES

By L. G. Cook

Corporate Research Staff, ESSO Research and Engineering, Linden, New Jersey

May 1973

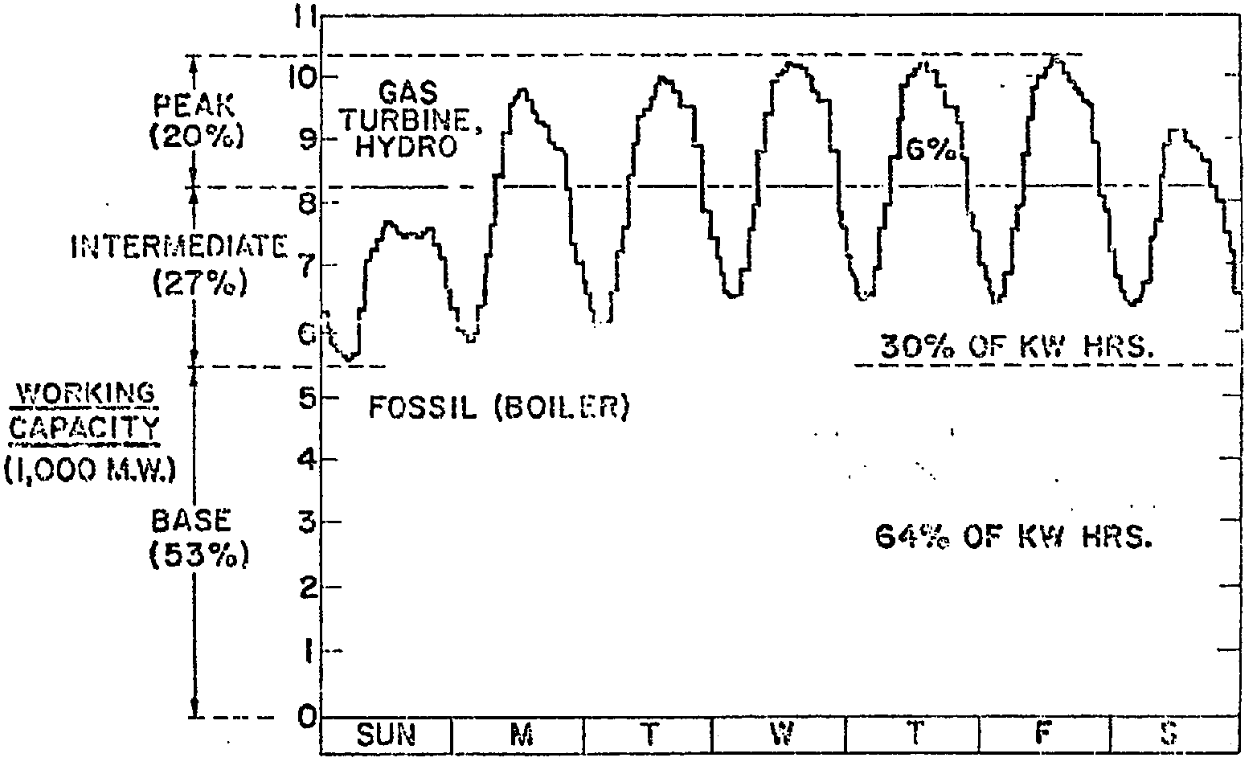
THE PATTERN OF THE PAST

The load pattern is a key determinant in the selection of generation technologies and in consequent fuel requirements. A typical composite weekly load pattern taken from the Federal Power Commission's 1970 National Power Survey report is shown in Figure 1.

FIGURE I

ELECTRICITY LOAD CURVE U.S.

(A TYPICAL UTILITY COMPOSITE EXAMPLE)



Up to the early 60's fossil fuel-fired under-boiler generating plants served in almost the whole range of load. New efficient plants were operated as nearly as possible full-time; older, less efficient, partially written off plants were used in the intermediate load range in which 12-14 hour operation 5 days a week is a sort of operational norm; still older, smaller plants would be placed on load only a few hours a day at the peaks. Hydro capacity, where available, was used near the peaks also because of its quick start-up capability.

During the 60's the technologies began to change. Gas turbines were increasingly installed to serve the peaks, backed up with hydro and pumped storage as shown in Figure 1. New fossil fuel plants for base load increasingly shifted to higher pressure* (so-called supercritical) technology for large plants (600 MW range).

Now in the 70's the next two major technology changes are occurring. Nuclear is growing into base load very rapidly; plants now existing and under construction will generate 50% of all base load power nationwide within 8-9 years (in several specific utilities, 100%); new base load high pressure* fossil capacity is still being installed although in decreasing amounts and will total over 80,000 MW at least by 1976. These two new types of specialized base load plant will be difficult if not impossible to demote eventually to intermediate load service proper. The thermal stresses caused by daily shutdowns are considered technically intolerable in supercritical fossil plants, and have to be assumed intolerable in nuclear plants also, unless and until experience proves otherwise.** Nuclear has another constraint upon it***--it is very capital intensive. For financial reasons alone, there will be every incentive to run nuclear capacity on a steady full load schedule, and great reluctance to use nuclear capacity directly in part-time intermediate load service.

It is evident that the intermediate load capacity growth requirement will soon be unable to be filled in historic fashion by demoting base load plants to part-time service; there will simply not be demotable plants available. A totally new technology pattern is emerging in which new plant capacity specifically designed for part-time intermediate load service must enter and expand rapidly. It is to identify this technology, its rate of entry and scale, and its fossil fuel implications that this report is addressed.

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* 3000 p.s.i. and over.

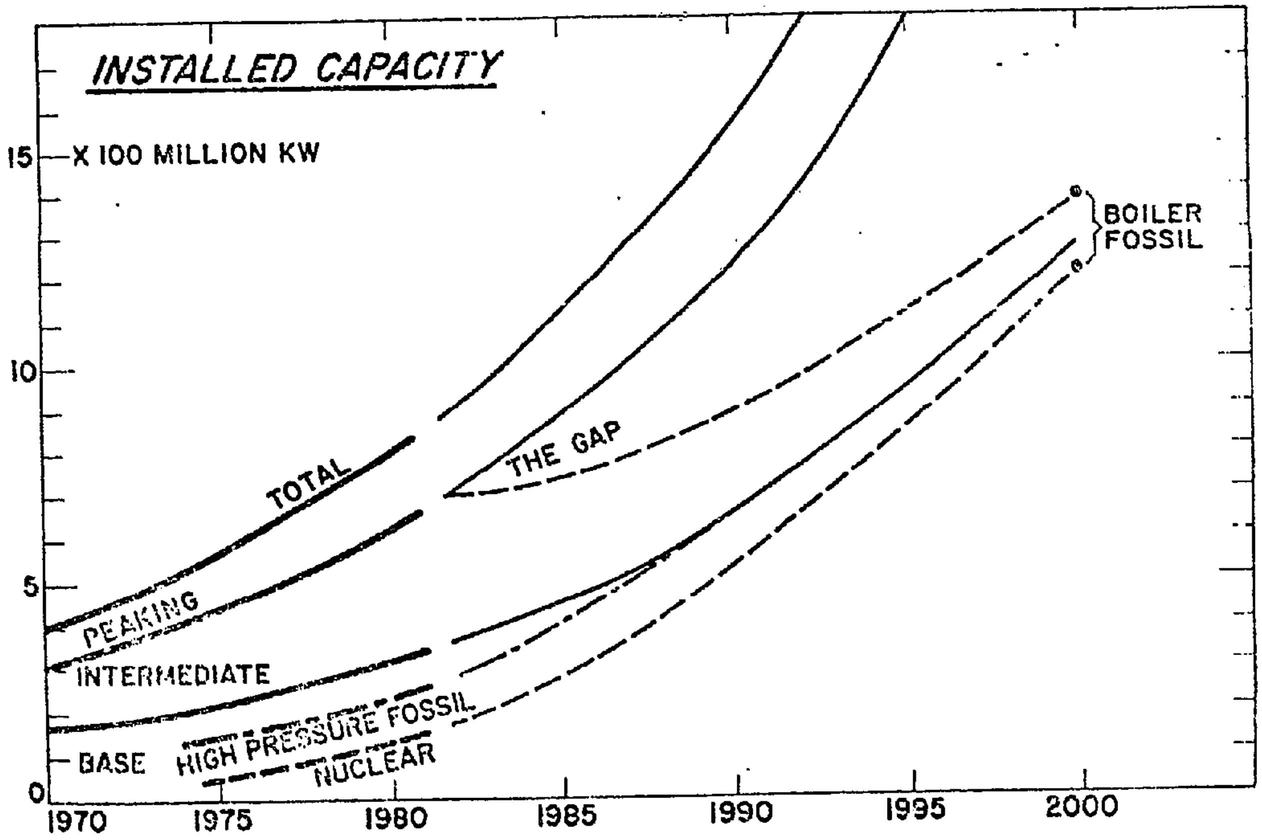
** In fossil plants it is the boiler and heavy sections in the turbines where thermal stresses are limiting.
In nuclear plants it is the fuel elements.

*** Editor's Note: Furthermore, in a large nuclear reactor, it may take 24 hours to adjust control rods so that neutron fluxes are leveled out in all parts of a freshly started reactor.

THE PATTERN OF THE FUTURE

The pattern of the future is shown in Figure 2. Up till 1981 the data is taken from the National Electric Reliability Council's Fall 1972 report of utility plans. Much of this capacity for 1981 is already existent or under construction (especially the nuclear and the high pressure supercritical fossil). These 1981 plans have been generally described to the author as "already cast in concrete" -- with 1985 already "poured" and "setting fast." The forward projection for nuclear is the most recent AEC estimate: the total capacity projection is simply a run-out at the historic 7%/year growth rate, divided into peaking, intermediate and base load in the same ratios as for the 70's.

FIGURE 2



Important aspects of this pattern are:

(1) Base load capacity will be 50% nuclear within 8-9 years and 75% within 15 years.

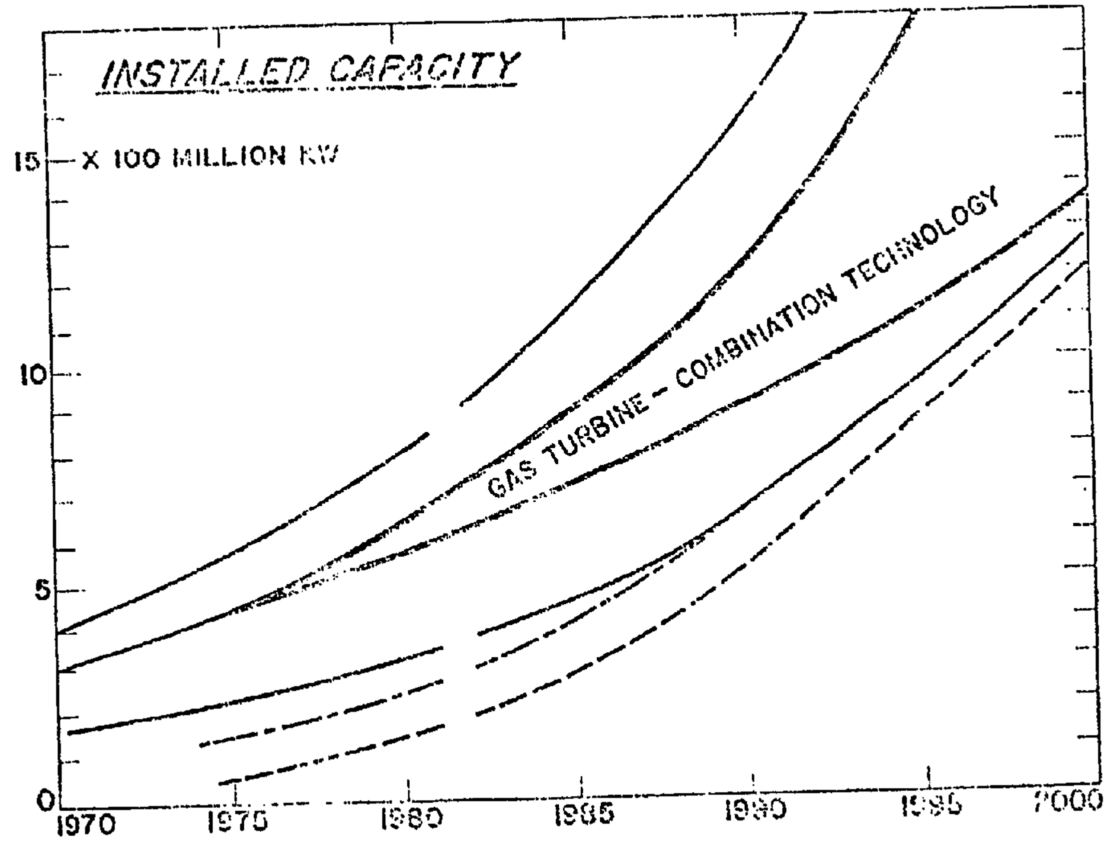
(2) Within 12-15 years (1985-1988) essentially all base load capacity will be of "nondemotable" types (i.e. nuclear and supercritical steam). From this point onward, all intermediate load capacity growth will have to be filled by the installation of new equipment-fuel systems specifically optimized for part-time service.

(3) This new type intermediate load capacity "GAP" begins to open in the early 80's.*

The technology which the electrical manufacturers have been grooming to sell to fill this "GAP" is the "gas turbine-steam turbine combination," also known as STAG (STeam And Gas Turbine) or PACE (Power At Combined Efficiency). A few oil-fired boilers have also recently been installed for this service. Whether this represents a trend or not, only time can tell.

Due to the delays in commissioning dates for new base load stations which have been caused in the last few years by "environmental" pressures, regulatory problems and construction delays, some utilities have decided to ensure themselves against a shortage of base load capacity in the mid-70's by beginning to order new "combo" units now, since they can be had with a 2-3 year delivery time. This movement began in 1972 when 6300 MW were placed on order. Since the forces which caused this advance ordering are continuing, a more realistic expectation for the "GAP" must place the capacity toe in 1974 instead of in 1981, as shown in Figure 3.

FIGURE 3



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* A basic assumption in this calculation is that the annual commissioning of new under-boiler type capacity for base load will drop to a negligible amount by 1981. This is the only assumption which is consistent with present technology trends, present ordering trends, and present utilities' planning. The validity of this assumption, and the consequences of various kinds of deviation, are explored in the Addendum.

This implied growth of gas turbine-steam turbine combination capacity is plotted directly in Figure 4.

FIGURE 4

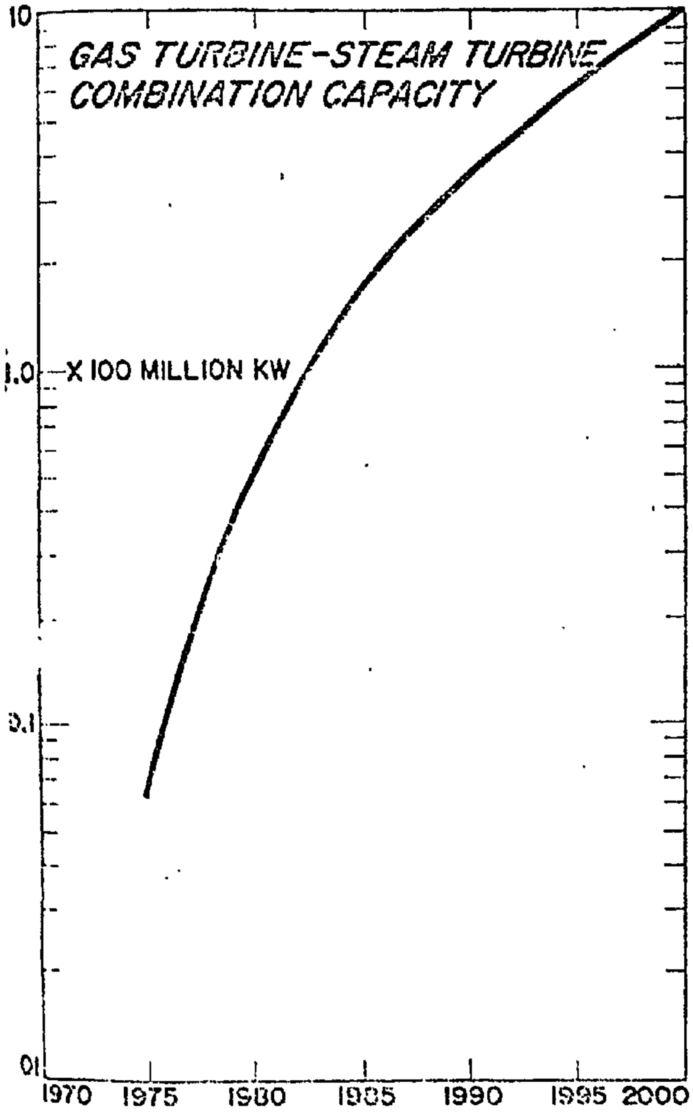
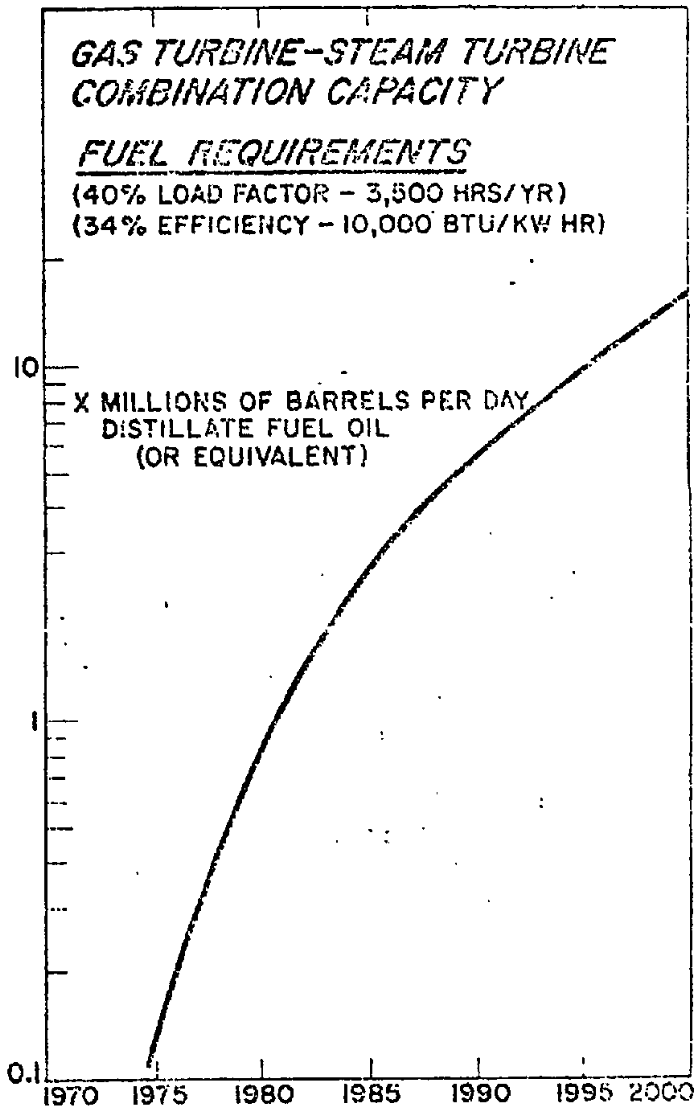


FIGURE 5



N.B.: The actual numbers from which Fig. 5 has been projected are as follows:
1968 25,000 bls/day 1973 200,000 bls/da
1969 33,000 (1974 300,000)
1970 68,000 (1977 1 million)
1971 92,000 of No.2 distillate
1972 150,000

THE FOSSIL FUEL CONSEQUENCES

The fossil fuel consequences of this changing electricity generation technology pattern are twofold:

(1) Under-boiler fuel requirements (crude, resids., coal) will peak in 7-8 years, and decline thereafter as old under-boiler capacity declines and is shifted to intermediate load service (Figure 2).

(2) Gas turbine quality fuel for intermediate load "combo" units will be needed in 1974, and the requirement will grow rapidly through 1985 (~ 30%/year) shading down in the 90's to ~ 12%/year.*

The magnitude of the fuel requirement for these new plants is shown in Figure 5 -- calculated on a basis of 40% utilization (3500 hrs./year) and 34% thermal efficiency (10,000 BTU/kwh heat rate).** The result is expressed in terms of distillate fuel oil (#2) because that is what the utilities are expecting to burn as the preferred and available fuel. (The alternate preferred fuel, natural gas, is generally anticipated not to be available for this use in the future.)

Adequately clean liquid or gas fuel can be prepared in other ways, some of which may well be more appropriate for such a large scale use. Crude oil can be burned directly if processed to remove those constituents harmful to gas turbines (especially sodium and vanadium, but also potassium and lead), and of environmental concern (especially sulfur). With low nitrogen distillate fuels, it appears that NO_x emissions are controllable by techniques such as water injection and careful combustion chamber design. With high nitrogen fuels, these control techniques would be less effective, and specially designed new control techniques would likely be required. Coal cannot be burned in gas turbines. Any serious consideration of the use of coal as a raw material base must include definition not only of the technology, but also of actual construction schedule commitments for the required mining and processing capacities to produce the required liquid or gaseous fuels to meet the time scale of need shown in Figure 5. At the present time there does not appear to be serious consideration of coal in this sense. Considering the lead times involved, this fuel requirement must be interpreted in terms of fuel oil at least through 1980--and, unless major new types of processing commitments are made very soon, through 1985 and 1990 as well.

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* If "clean oil"-fired boiler units should take a share, the fuel oil requirement still remains; so this possible alternative will not be further specifically mentioned. For further elucidation, see the addendum to this report, Question 10, Page 18.

** Present "combo" units have a heat rate 10% lower than this; gas turbines used alone have a heat rate 25% higher; in many utilities, gas turbines alone are being used in intermediate load schedules now. Future "combo" units are planned to use higher input temperatures and be more efficient. Including all the "ifs," "ands" and "buts," the figures used should be correct--give or take 25%.

Conclusions are:

1. The take-over of base load by high pressure fossil and nuclear will result in a rapidly increasing commitment to oil-fired equipment for intermediate load. The current trend is strongly to gas turbines, although oil-fired boilers are thought to be competitive in principle.
2. As this commitment develops, the utilities' requirements for fossil fuels will shift from residuals and coal to clean fuels. The potential requirement will reach 1 million B/D fuel oil equivalent by 1980, 3 million by 1985, and 6 million by 1990.
3. Longer range alternatives to clean fossil fuels for intermediate load include direct load following by nuclear (which is costly because of the high capital investment), and nuclear-based energy storage systems. These are coming under intensive consideration by utilities, but are unlikely to be in extensive use before the mid- to late 80's.
4. Gas turbines in this service presently use gas or distillate fuel oil (#2 or kerosene). Neither fuel is likely to retain this market. Natural gas is in short supply; synthetic natural gas will be costly; low BTU fuel gas is difficult and expensive to adapt to a part-time service; and distillate fuel oil is of unnecessarily high quality.

Technical Implications are:

Pressure to use domestic hydrocarbons, especially coal, as the basic raw material source for these clean fuels through the next 20-30 years must increase.

SPECTROSCOPIC TECHNIQUES IN CATALYSIS

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Catalytic chemists used to dream about being able to look at catalytic surfaces to see what is going on. Today the dream is a lot closer to reality since over the past 15 to 20 years practically every form of spectroscopy has been applied to catalyst surfaces, leading to very real gains in understanding. At the same time, of course, many complexities have appeared that we suspected were there, which we are going to have to face. As Bob Burwell pointed out yesterday, catalysis is as broad as chemistry. The particular kind of spectroscopic technique chosen depends very much on what sort of a catalyst and what catalyst surface is being analyzed. The techniques that are applicable for surfaces of high-area oxide catalysts or of supported metals such as used in petroleum refining are not necessarily the ideal techniques to use in fuel cell catalysis. I'm obviously not going to have time to cover all these kinds of spectroscopy, so the work that I will discuss is primarily my own, primarily infrared spectroscopy. I will try to give at least a thumbnail sketch of some of the other possibilities. The use of infrared spectroscopy in surface studies in this country dates back to the work of Bob Eischens at Texaco, started about 1955. Infrared has been applied much more extensively than any other spectroscopic technique. There have been two books written on the subject which can provide further background.

There are various ways in which infrared can be applied. These are shown, in part, on the first slide. Normally, in most of the work on high area catalysts, conventional transmission-infrared-spectroscopy is used, in the same way that infrared spectroscopy is generally used, subject to the same limitations and to a few additional ones created by the use of high area adsorbants. In order to get useful spectra from surface groups and adsorbed molecules, an effective thickness of about 1,000 molecules is typically required in the infrared beam. This is readily effected with high area adsorbants or catalysts. There is no problem with typical refinery catalysts, because these have surface areas of 100 square meters per gram or more. It's quite feasible to study adsorbed molecules or supported metals on real catalysts at less than 1% monolayer coverage. Multiple reflection from single crystal metal surfaces provides an alternative approach, but is practically limited to well under 100 reflections. There have been effective studies made of adsorbed molecules with direct reflection studies. Greenler, at Wisconsin, has published work in this area. Multiple internal reflection is more efficient than direct reflection in surface studies and has been applied even to fuel cell electrodes, using germanium for an internal reflection element, getting up to perhaps 100 reflections. Multiple scan interferometry is another method which is capable of high sensitivity which in the future will probably make studies on low area catalysts feasible. Although, the last three techniques are not widely used at the moment, they should be recognized as capable of further development. What sort of information can we get out of infrared? The next slide will indicate areas that are quite accessible to infrared study with present techniques on high-area catalysts. On oxide catalysts, we are normally dealing with surface hydroxyl groups. These can differ in chemical properties and in catalytic importance. The removal of these hydroxyl groups can create sites on the surface, which are highly polar and capable of catalyzing certain reactions. Other surface groups can also exist on oxide catalysts, like NH_2 groups or carbonate groups, or nitrate, sulfate, so on. These groups can all be studied with present techniques. Adsorbed reactants or products are also reasonable subjects for present study and a lot of work has been done in this area. Using molecular probes like carbon monoxide, ammonia, carbon dioxide, pyridine, it is possible, through changes in the spectra of these materials, to analyze the nature of the sites on which these probes are adsorbed. Methods using molecular probes can reveal information about surface sites that are not directly accessible to infrared study and about supported transition metals. Supported platinum and nickel for example, have been studied by probes, and differences can be seen in the oxidation states and the metal surface areas or the effective exposures of these elements on a catalyst surface. Surface acid sites can be revealed and characterized for example, by adsorption of ammonia. Adsorption of ammonia as NH_4^+ ions indicates interaction with a surface proton; adsorption as NH_3 occurs on Lewis acid sites. Ammonia may act as an acid and give a proton to the surface and attach an amine group. "Strained surface bonds" may reflect incompletely coordinated oxide ions in the surface or bonds that are somewhat deformed and more reactive than others. Such bonds can, in time, react with adsorbed molecules to form groups that would not normally be expected on the surface. As an example, the next slide shows, on alumina, which is one of the most important catalyst supports, some of the surface hydroxyl groups that are possible. We have three principle types which vary in relative numbers as the surface is progressively dried, at drying temperatures of 700, 800 and 900 degrees Centigrade. Originally, there were about five different types of groups, and ultimately after drying at high temperatures there are mainly three types remaining. These on the right are double-beam spectra to show the changes clearly without the water vapor in the background. The hydroxyl groups differ in their chemical properties, but it's not known what these differences are due to. I think that they reflect differences in the local environment of hydroxyl groups on a single crystal face of alumina. But the hydroxyl groups are non-hydrogen bonded groups differently attached to the surface, whether on one crystal face or several, and they differ in chemical properties. As shown in the next slide we can adsorb ammonia to obtain further information. We see here the three original hydroxyl groups after the sample has been dried at 800°C. For the lower spectrum there is one ammonia molecule for every 40 square Angstroms, affecting the hydroxyl bands at high and low frequencies and causing them to disappear. These NH stretching bands are produced from the adsorbed ammonia. When the ammonia is subsequently desorbed, at 400°C, we get certain changes in the spectrum of the adsorbed ammonia, in the stretching region. We also see changes in the NH bending deformation region, and, at the same time, get an increase in one type of OH group. The primary conclusion is that at certain sites, created by the removal of hydroxyl groups, ammonia can form both new OH groups and NH_2 groups attached to the surface. There are other bands that support this conclusion. The sites on which this occurs include the sites on which butene undergoes double bond isomerization. These occupy about 5% of the surface. The next slide shows the adsorption of carbon dioxide as a probe on alumina. If carbon dioxide is adsorbed on alumina, dried at high temperatures, a series of bands appear in this region due to surface carbonates. The carbon dioxide can be held strongly or weakly. These two curves represent bands produced at different equilibrium pressures. In addition to these so-called carbonate bands, there is a band due to strongly adsorbed carbon dioxide, held with about 15 kilocalories of energy per mole, at around 2350-70 cm^{-1} and another CO_2 band which would not normally appear in infrared, but only in Raman, down here. When the surface oxide is replaced with fluoride, all these oxide sites that form carbonate are removed and we see no more carbonate bands when CO_2 is subsequently adsorbed. But we still have this type of adsorption site that holds the CO_2 as such. These sites are believed to be exposed aluminum ions adjoining some sort of an anion, namely, in the first case, an oxide ion and, after fluoriding, a fluoride ion. So, there is a slight shift in the frequency of this band, indicating an alteration in the nature of the acid site as a result of replacing oxide by fluoride. The last infrared spectrum is an example of a real mess. When NO is used as a probe molecule on a chromia-alumina sample, there results this series of bands, about seven of them, all of which represent NO coordinatively bound to exposed Cr^{+2} or Cr^{+3} ions in the surface. The way in which it's held and the way in which these adsorbing sites change as the sample is reduced, may all be studied by careful systematic variation of the reduction conditions and of the concentration of chromia on the surface, and assignments may be made for these different bands. Eventually, a much simpler picture results where essentially only two bands remain. These are from NO or Cr^{+2} ions. But I won't go into the other assignments. Well, catalysts of this sort, with chromium molybdenum, nickel or other transition metals ions on the surface can be very important in oxidation auto catalysts, and in desulfurization in the case of molybdenum or cobalt. Variations in the surface properties are quite easily and effectively studied. Let's look at some other techniques that have been used. Raman spectroscopy is theoretically an ideal supplement for infrared. With the advent of laser Raman, it's also become more practical. There have been maybe a dozen studies made using laser Raman, but, so far, it's not as important as infrared. Inelastic scattering of cold neutrons offers information in regions of the spectrum which are not accessible through infrared study of oxide catalysts, but it requires a nuclear reactor so it's not everybody's ball game. Visible and ultraviolet spectroscopy are applicable in certain cases. Electron spin resonance has probably been used more widely than any other spectroscopic technique except infrared, and is applicable to transition metal ions with one or more unpaired electrons or to adsorbed free radicals. NMR has not been much used in catalyst studies, because there are relatively few nuclei that are accessible to this sort of study and, furthermore, serious broadening occurs when molecules are held immobile on the surfaces. Al^{27}, protons, and fluorine have been studied, but that's about it. Mössbauer spectroscopy is also valuable in some cases but not applicable to many elements. Finally, electron spectroscopy has been getting a lot of attention recently. This has been called various things, such as photoelectron spectroscopy or electron spectroscopy for chemical analysis. A slightly different variation is Auger spectroscopy. All are capable of yielding valuable information. The final slide, which I've taken from Delgas' work, shows application of x-ray photoelectron spectroscopy to the surface of a single crystal of nickel exposing the 111 face. This peak is due to metallic nickel, and this second peak as well as another peak seen here on nickel oxide is due to nickel (I think that this peak was described as Ni^{2+}, and this peak very tentatively to Ni^{3+}). You can see that when nickel foil is sanded you remove an oxide film which is present on nickel foil off the shelf. Spectra of this sort do not have as high resolution as infrared or many other forms of spectroscopy are capable of yielding, but theoretically one can get information about nearly all elements this way. This technique is being widely applied and should be of immense value in many future catalyst studies.

I have tried to cover a lot of material. I have some references available on all these techniques for those of you who are interested in pursuing any of them further. Again, the techniques that can be used will depend on the particular systems to be studied. Generally, not all techniques are applicable, but all those that are would ideally be used in any one case. There are certain practical limitations, as we are all aware, but I think that much more can be done, and much more can be learned. If research support is available, the future of catalysis is going to look much brighter than it does at the moment.

Discussion:

Suhl: In the case of electron paramagnetic resonance and nuclear resonance measurements, can one measure a monolayer or is that too difficult?

Peri: Particularly electron spin resonance is very sensitive, and one can work with very small fractions of a monolayer.

Hightower: Less than a tenth of one percent, Professor Boudart says, 10^{-6} of a monolayer.

Rabo: Some reactants can distinquish between spin resonance phenomena on the surface and that underneath by affecting those electrons which are right on the surface and in this way one can distinquish surface phenomena from bulk phenomena.

Wise: In response to Dr. Suhl's question, to distinquish surface free radicals or unpaired electrons is a very difficult problem in ESR. With adsorption techniques, such species as O^-, $O^=$, O^- may be present as an adsorbate but there's debate in literature as to what the signals represent, in terms of identification of species.

Heinemann: Many techniques have been developed to look at catalyst surfaces. What is seen with one technique on a specific catalyst may or may not be the same as seen with a different technique on a different catalyst. The science of catalysis could be furthered if all spectroscopic and other techniques of looking at catalyst surfaces could be systematically applied to the same samples so that corelationships between various measurements on the same

Heinemann: (Continued)

sample would be available. This requires on the one hand a catalyst bank, a storehouse of samples of available catalysts which can be made available to workers in various fields and in various places; and secondly, it requires a coordinated effort, in which people use the same samples in different studies. This requires money.

Worley: What pressure conditions exist in these various experiments you have described?

Peri: Most of the work was done at atmospheric pressure or below, say a few millimeters. However, in some cases we used a high pressure cell at up to several thousand pounds, at realistic catalytic refining conditions.

Worley: Yes, that's one approach, but to understand the surface one should work at 10^{-10} torr.

Peri: No, now wait a minute. What is really going on on the surface under what conditions?

Worley: Well, how do you make sure the surface is clean, how do you know what's on the surface?

Peri: A surface for catalytic purposes might be a lot "cleaner" in say a reforming reactor with high hydrogen pressure than it is in 10^{-10} Torr vacuum.

Burwell: One might characterize various techniques as being physical-chemistry or chemical physics techniques. With spectroscopic or the physical chemistry

Burwell (Continued)

techniques one can make measurements representative of practical conditions of catalysis. On the other hand, measurements by photoelectron spectroscopy for example require low pressures. Consequently, there is required a large extrapolation to pressure of practical catalytic interest. Furthermore, many chemical-physics techniques are rather energetic like probing peanuts by throwing six inch shells at them. With thousand volt electrons one must be careful to see that he is not destroying what he is trying to measure.

Lauriente: I was involved in airline security developing sensitive bomb sniffers. One of the new instruments that we considered was ion-molecular spectroscopy and it has several other names. It is a type of spectroscopy that works at ambient pressures. I call it a dirty mass spec. But there is still a lot of research required to analyze the signatures that one gets with this type of instrument. The usual mass spectroscope requires high vacua so that if you are trying to find out fundamental mechanisms sometimes the operation will be a success, but the patient dies.

Hightower: Do you know if that technique has been applied to surfaces?

Lauriente: Oh, yes.

Hall: I'd like to comment on this infrared spectroscopy as applied to the Defense Department needs. Most of these adsorbents have very high surface areas. And they have the ability to adsorb many different kinds of molecules. In this way very small quantities of material become visible in the infrared; there are unlimited possibilities for detection devices of the type mentioned.

p

Libby: There's a technique not mentioned, namely, nuclear gamma ray excitation by particle beams. This is exceedingly powerful, with very low limits for those nuclei which have distinct gamma rays.

Peri: As a general statement, almost every form of spectroscopy has been applied and for special cases it can be very valuable.

Worley: What about this inelastic tunneling spectroscopy of Weinberg?

Peri: This has a limitation in that it requires making a sandwich with a layer of lead or the like on top which creates problems in catalytic studies, but does seem to be interesting and exciting.

Worley: He claims that he can get better resolution for the same information as from infrared.

Peri: I'm going to talk with him tomorrow morning.

Worley: I'm going to talk to him tonight.

INFRARED SPECTROSCOPY IN SURFACE STUDIES

1. CONVENTIONAL TRANSMISSION
   (HIGH–AREA ADSORBENTS AND CATALYSTS)
2. MULTIPLE REFLECTION
   (LOW–AREA METALS)
3. MULTIPLE INTERNAL REFLECTION
   (LOW–AREA SOLIDS, TRANSPARENT TO IR)
4. MULTIPLE SCAN INTERFEROMETRY

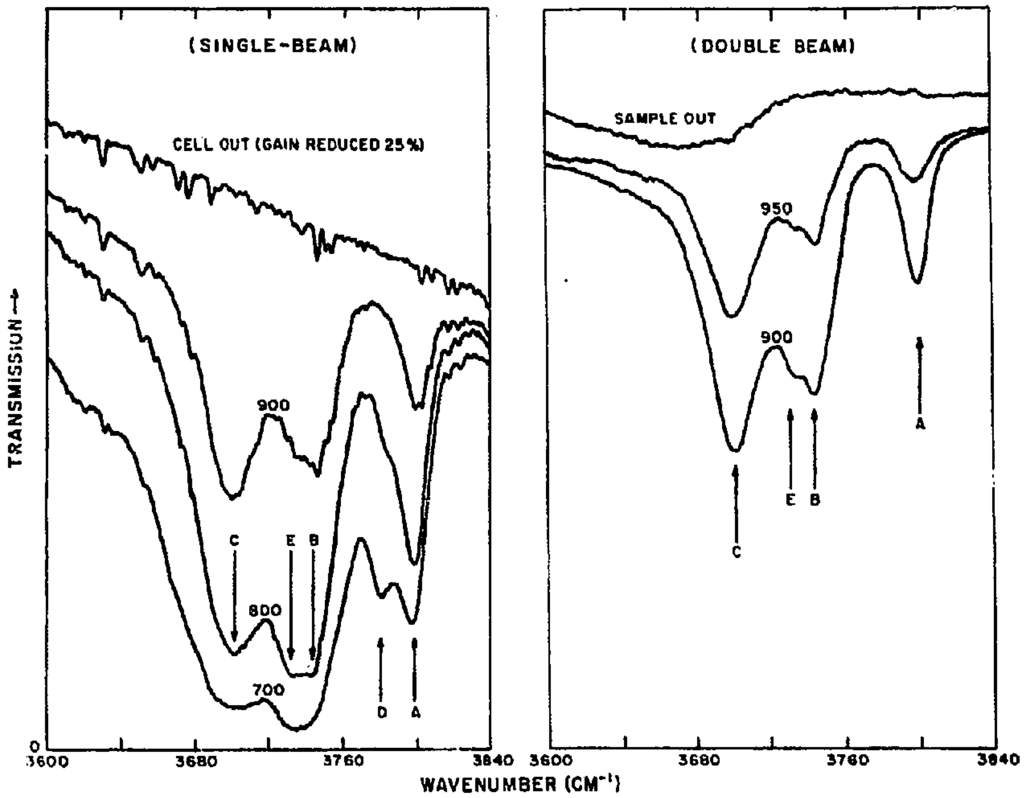
INFRARED SPECTROSCOPY IN CATALYST STUDIES

A. DIRECT STUDY

1. SURFACE HYDROXYL GROUPS
2. OTHER SURFACE GROUPS (NH$_2$, CO$_3^=$, ETC.)
3. ADSORBED REACTANTS AND/OR PRODUCTS

B. INDIRECT STUDY–USING "MOLECULAR PROBES"

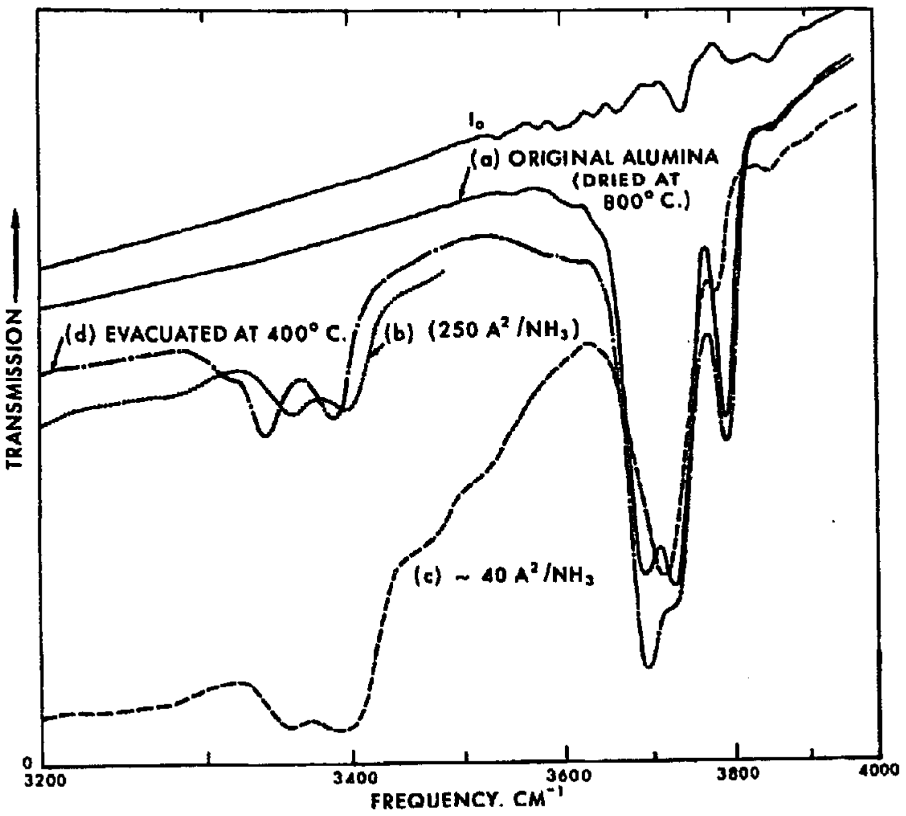
1. SUPPORTED TRANSITION METALS
2. SURFACE "ACID" SITES
3. "STRAINED" SURFACE BONDS



SPECTRA OF ALUMINA DRIED AT INDICATED TEMPERATURES (°C)

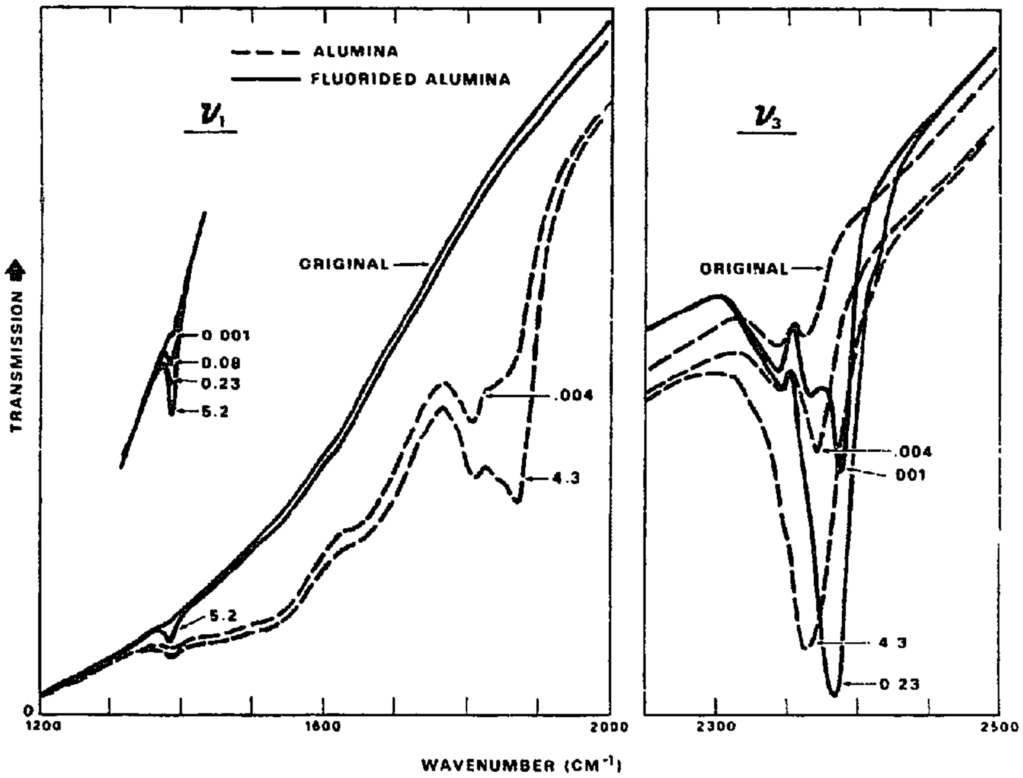
3

ADSORPTION OF NH₃ ON ALUMINA



4

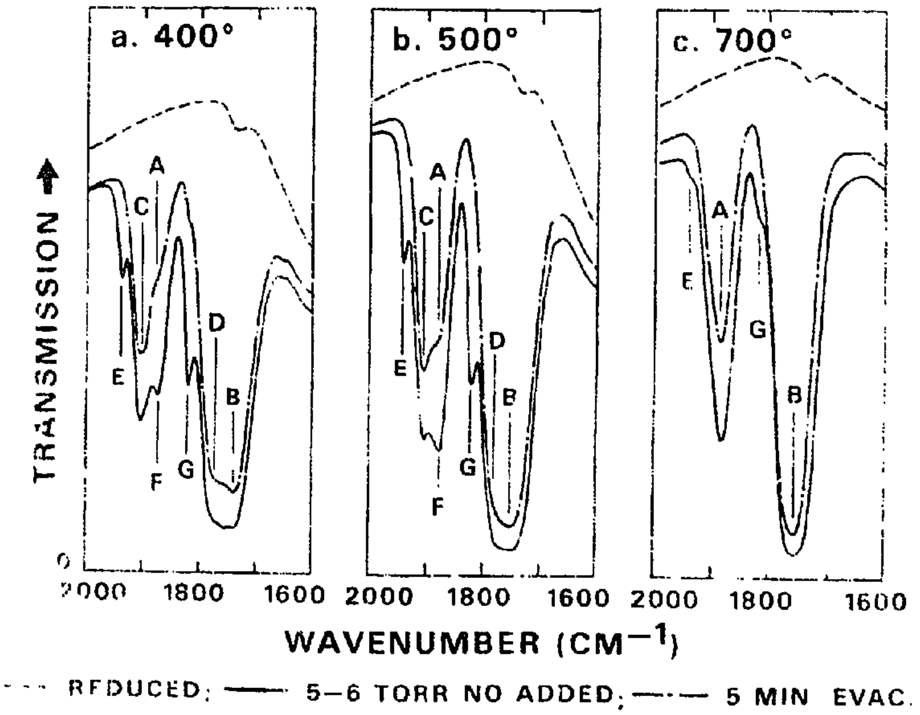
CO$_2$ ON ALUMINA AND FLUORIDED ALUMINA



5

ADSORBED NO ON 10% CrO$_3$/Al$_2$O$_3$

(REDUCED AT INDICATED TEMP., °C)



6

OTHER TECHNIQUES FOR CATALYST SURFACE STUDIES

1. RAMAN SPECTROSCOPY (LASER–RAMAN)
2. INELASTIC SCATTERING OF COLD NEUTRONS
3. VISIBLE AND ULTRAVIOLET SPECTROSCOPY
4. ELECTRON SPIN RESONANCE (ESR)
5. NUCLEAR MAGNETIC RESONANCE (NMR)
6. MÖSSBAUER SPECTROSCOPY
7. ELECTRON SPECTROSCOPY (EPS–ESCA, AUGER)

X-RAY PHOTOELECTRON SPECTROSCOPY

W. N. DELGASS,
T. R. HUGHES
AND C. S. FADLEY
(1970)