Chapter 6

CATALYSIS FOR INDUSTRIAL CHEMICALS J. E. Lyons and G. W. Parshall

6.1 INTRODUCTION

The chemical industry in the U. S. produces a spectrum of materials that find their way into all other industries and into products used in every household. The industry employs about 1.2 million workers. These individuals produce about \$140 billion worth of materials ranging from household detergents to pharmaceuticals to polymer-based plastics, fibers, and films.

A major segment of the chemical industry business is an array of about thirty organic chemicals and polymers that are used in applications that touch our lives daily. These remicals are produced on a huge scale (Tables 1 and 2) and, collectively, are worth over \$60 billion. They are largely commodities produced to meet standard specifications and are sold primarily on the basis of price. Because the scale of production is so large, they are a major factor in the chemical industry's effort to develop manufacturing technology that meets the environmental expectations of modern society.

Catalysis is a major technology used in the manufacture of commodity chemicals. The chemicals produced by catalytic processes are highlighted in Tables 1 and 2. In addition to these organic chemicals and polymers, the two largest scale inorganic chemicals, sulfuric acid (88.6 billion ppy) and ammonia (34.0 billion ppy), are produced by catalytic processes. Catalytic technology is a key to both the economic competitiveness and the environmental acceptability of this major sector of the American economy. Looking to the future, catalysis can also play a significant role in sustaining this industry by providing the technology to use feedstocks other than petroleum and natural gas. Heterogeneous catalysis in particular will be critical in processes to utilize abundant raw materials like coal and renewable biomass-derived feedstocks.

In this chapter we seek to define research objectives in heterogeneous catalysis which, if achieved, will enable the production of major industrial chemicals with greater energy and feedstock efficiency and with improved environmental friendliness. We outline both current manufacturing processes and potentially advantageous advanced technologies that may improve the ways that commodity chemicals and polymers are produced Based on input from experts in industrial heterogeneous catalysis, we identify potential technologies from which advanced manufacturing processes may be developed. These technological goals, in turn, define research objectives that may be appropriate subjects for consideration. The essential research needs are prioritized in Section 6.4.

Table 1.

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1991 U. S. Production of Major Organic Chemicals Products made by catalytic processes shown in holding

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PRODUCT	J. S. PRODUCT	VALUE (\$ billions)**	
Ethylene	39.23		8.23
Propylene	22.02		3.30
Benzene/toluene	18.58		2.41
Ethylidenedich/oride/vinyl chloride	13.92	(11.7)	1.70
Methyi t-butyi ether	9.60		1.73
Ethylbenzenc/styrene	9.22	(9.01)	2.16
Methanol	8.65		0.58
Terephthalic acid/dimethyl terephthal	ate 7.66		2.30***
Formaldehyde (37%)	6.43		0.71
p-Xylene	5.43		1.11 ·
Ethylene oxide/giycol	5.24	(4.93)	2.36
Cumene/phenol/acetone	4.28	(3.49/2.13)	1.69
Acetic acid	3.61		1.19
Butadiene (polymer grade)	2.91		0.55
Propylene oxide	2.75		1.58
Acrylonitrile	2.65		0.93
Vinyl acetate	2.65		1.17
Cyclobexane	2.31		0.39
Adipic acid	1.56		1.09
n-Butanol	1. *1		0.52
Isopropanol	1 30		0.47
Caprolactam	1.28		1.14
TOTAL	172.59		37.31

۰ Chemical and Engineering News, June 1992

** Chemical Marketing Reporter, November 1992 *** Industry sources

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Polymer	Production (billions of pounds)	Value (\$ billions)	
Polyethylene* (low dens.)	11.58	3.94	
Polypropylene	10.20	3.67	
Polyethylene (high dens.)	9.22	3.13	
Polyvinyl chloride	. 9.17	2.38	
Polyester	5.52	3.64	
Polystyrene	4.96	2.03	
Nylon *	3.11	3.89	
Phenolics	2.66	1.3	
ABS	2.29	1.42	
TOTAL	58.71	25.40	

Table 2.	
1991 U. S. Production of Major Synthetic Polymers.	(Sources as in Table 1.)

* Prepared partially by catalytic processes. Polymers in bold face made entirely catalytically.

6.2 COMMODITY CHEMICALS AND POLYMER INTERMEDIATES

Essentially all the highlighted chemicals in Table 1 are manufactured by well established catalytic processes. Some of the processes are very efficient in their use of energy and feedstocks and offer only modest incentives for research in catalysis. For example, the manufacture of acetic acid by carboxylation of methanol proceeds in nearly quantitative yield under mild processing conditions (Parshall, 1992). The source of both the methanol and the CO used in this process is synthesis gas (CO/H2), which may be made from almost any hydrocarbon or, potentially, from biomass. Although improved catalysts may play a role in better processes for methanol and synthesis gas (Mills, 1993), only incremental opportunities exist for improving the synthesis of acetic acid or its derivatives. These improvements are likely to be achieved through advances in engineering rather than through fundamental studies in catalysis.

In contrast to the efficiency of the methanol carboxylation process, many other catalytic processes to make the chemicals in Table 1 offer great scope for improvement. Some of the potential incentives are:

- Improvement in utilization of a current feedstock, particularly petroleum. The opportunities for improvement are especially great for oxidation processes. Generally, an improvement in feedstock utilization yields environmental cenefits such as reduced waste production and pollution.
- Substitution of an abundant or renewable feedstock. The benefits are most substantial for petroleum-based chemicals such as adipic acid and caprolactam.
- Reduction of severity of reaction conditions. The attendant reduction in energy consumption saves fuel and reduces the output of carbon dioxide, a major contributor to global warming.
- Reduced production of toxic, corrosive, or environmentally damaging chemicals and by-products. The incentives are especially great for reduction of halogen- and nitrogen-containing by-products in the manufacture of nitriles and CFC replacements.

Each of these areas is discussed below along with recommendations for technology development and research needed to capitalize on the opportunity.

6.2.1 Utilization of Current Feedstocks

The chemical industry has a huge infrastructure of process facilities based on petroleum feedstocks. Ultimately, these facilities are likely to be replaced by new generations of plants based on abundant or renewable feedstocks, but the cost in time and capital to replace the existing plants dictates that major changes in feedstocks have to occur gradually over a period of decades. (The conversion of vinyl monomer technology from acetylene to olefin feedstocks is instructive. Even though acetylene is expensive in both dollars and energy, some acetylene-based plants are still operating thirty years after the introduction of catalytic processes to make vinyl acetate and acetaldehyde from ethylene.) As a result, improvements in current processes through the use of better catalysts can lead to substantial savings in the use of feedstocks such as petroleum. These savings can support the competitiveness of American industry and promote energy independence.

6.2.1.1 Oxidation Processes

Probably the largest area for improved feedstock utilization is in the oxidation of hydrocarbons to alcohols, ketone, epoxides, and carboxylic acid derivatives, as illustrated in Figure 1. The yields of many oxidations, especially those based on free radical processes, leave much to be desired.

The oxidation of cyclohexane to cyclohexanol and cyclohexanone, which are major intermediates for making adipic acid and caprolactam, generally proceeds in 70-80% yield. The subsequent oxidation to adipic acid using nitric acid as an oxidant gives very high yields, but produces nitrous oxide, an atmospheric pollutant, as a byproduct. The conversion of cyclohexanone to caprolactam by conventional technology yields massive amounts of ammonitim sulfate as a low value coproduct.



Figure 1. New Catalysts Have the Potential to Simplify Current Multistep Processes to Single-Step, Energy-Efficient Transformations of Alkanes to Commodity Chemicals.

- The homogeneous catalytic oxidation of butane to acetic acid is still carried out on a very large scale even mough the yield of the desired product is only 45-50%. Some formic and propionic acids are also recovered, but the production of carbon oxides as byproducts is substantial. They arise both directly from the oxidation and from the energy production for the extensive distillation needed to separate the carboxylic acids.
- ► The oxidation of butane to maleic anhydride also gives low (ca. 50%) yields in conventional heterogeneous catalytic processes but, in contrast to the acetic acid process, there is little recovery of other useful products. The main coproducts are carbon oxides.

- The oxidation of ethylene to ethylene oxide occurs in 85-90% yield, but the coproduction of carbon oxides is substantial because the process is conducted on such a large scale.
- Another major class of industrial oxidations is the two-step heterogeneous catalytic production of either acrylic acid from propylene (overall yield > 85%) or methacrylic acid from isobutylene, also in high yield. The combined production of acrylate and methacrylate monomers from these catalytic technologies exceeds one billion pounds per year in the U. S. alone.

Other important large-scale oxidation processes (Table 1) include the heterogeneous catalytic oxidation of methanol to formaldehyde, the homogeneous catalytic oxidation of p-xylene to terephthalic acid, and the epoxidations of propylene to propylene oxide, which can employ either heterogeneous or homogeneous catalysts. Since these three processes are over 95% selective to the desired products, there is less room for improvement in their catalytic reaction chemistry than in those oxidations mentioned above.

In all the highlighted examples, catalyst improvements can lead to greater selectivity in the formation of desired products with attendant economic and social benefits. More selective conversion of hydrocarbon feedstocks clearly reduces the consumption of valuable hydrocarbon resources. It also reduces energy consumption in product purification, typically by distillation. The reduction in by-products minimizes waste disposal problems. When the by-product is carbon dioxide, as in the oxidation of butane to maleic anhydride, the global warming potential is reduced.

6.2.1.2 Advanced Oxidation Processes

Hydrocarbon Feedstocks — Because the cost of feedstocks can be as much as 60-70% of manufacturing costs, a very direct way to lower the cost of making a commodity chemical is to find a way to use a less costly raw material. The feedstocks for most commodity chemicals and polymers are olefins or aromatics. Much of the cost of these materials arises from the high temperature endothermic processes (reforming, dehydrogenation, cracking) to make them from less expensive saturated hydrocarbons, as shown in Table 3. As shown in Figure 1 above, many current processes start with an energy-intensive endothermic step that produces an unsaturated feedstock which, in turn, undergoes a reaction to introduce a functional group into the molecule.

Multifunctional Catalysts to Transform Aliphatic Feedstocks — Figure 1 shows potential new developments in multifunctional catalysts that could do both steps in transforming an alkane into a functionalized commodity chemical. One current system mentioned in 6.2.1.1 is that in which butane is dehydrogenated, exidized, and cyclized to produce maleic anhydride in a single catalytic process. The formation of an unusually stable five-membered cyclic anhydride is among the driving forces for the technical success of this reaction. Although the reaction has been practiced commercially for some time, it is still being improved significantly (Stadig, 1992; Centi, 1993).

	MMM Lb/Yr*	Manufacture
Olefins		
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Ethviene	39.2	Alkane Cracking
Propylene	22.0	Dehydrogenation
Isobutylene	(n.a.)	Dehydrogenation
Styrene	9.0	Dehydrogenation
Butadiene	2.9	Dehydrogenation
Aromatics		
Benzene	11.8	Reforming, dealkylation
Toluene	6.8	Reforming, hydroforming
Xylenes	6.5	Reforming
Ethylbenzene	9.2	Alkylation, reforming
Cunene	4.3	Alkylation, reforming

	Table 3.		
Production of Hydrocarbon	Monomers for	Fuels and	Chemicals.

* Chemical and Engineering News, June 1992.

Acrylic and methacrylic acids are currently produced from relatively costly olefins (Figure 1). Recent work is pointing the way to multifunctional heterogeneous catalysts that promote direct exothermic reactions between the respective alkanes and dioxygen to produce these acids in a single step (Ai, 1992; Kuroda, 1992). Early results, though promising, have not yet produced the selectivities needed for a commercial process. Continued work could revolutionize this area of catalytic oxidation. It would be extremely valuable to understand the role of each of the many metallic ions added to the basic metal oxide structure of the c-tidation catalysts (Gellinga, 1992). New catalyst characterization tools like those discussed in Chapter 3 could be very helpful in this regard.

As with the acrylic and methacrylic acid processes, direct air oxidation of methane to methanol or formaldehyde would be valuable for conservation of both energy and hydrocarbon feedstocks. The direct oxidation would obviate the need for discrete steam reforming and methanol synthesis steps (Kennedy, 1992). Direct ammoxidation of propane to acrylonitrile has also been achieved in modest yields on a laboratory scale (Centi, 1992). Development of practical catalysts for such one-step reactions will eliminate costly two-step routes with energy-intensive, endothermic, initial steps, and will produce energy as a valuable by-product of the exothermic one-step processes.

Alcohols from the Selective Oxidation of Alkanes -- Alcohols such as methanol, ethanol, isopropanol, and tert-butyl alcohol are produced in enormous quantities today (Table 1). Direct oxidation of the light alkanes present in natural gas and in low-value refinery streams would be a valuable addition to current chemical process technology. Despite extensive research on teactions such as the selective oxidation of methane to methanol mentioned above, there are no commercially practical catalysts that have the required selectivity. Instead, alcohols are produced by traditional two-step processes in which an initial energy-consuming first step generates a reactive intermediate which is then converted to the alcohol in a second process step, as illustrated in Figure 2.

Methane to Methanol



Propane to isopropyl Alcohol



isobutane to t-Butvi Alcohol



Figure 2. New Catalysts Can Provide Direct Processes for Alternative Motor Fuels and Reformulated Gasolines. Recent research, drawing on experience in enzymatic and homogeneous catalysis, provides clues to the design of heterogeneous catalysts that may have the necessary selectivity to make one-step oxidations of alkanes to alcohols commercially feasible. For example, "design catalysts" with oxo centers on the surfaces could be patterned after enzymatic species that are selective for alkane oxidation (Lyons, 1991). In another recent development, highly electrophilic metal centers catalyze selective oxidations such as the liquid phase oxidation of methane to methanol (Periana, 1993). Heterogeneous catalysts embodying these principles could exhibit enzyme-like selectivity while affording practical benefits, such as process simplicity, easy product recovery, and low corrosivity.

Other examples of multistep processes to produce commodity chemicals include the manufacture of phenol, ethylene glycol and propylene glycol. New processes for the direct hydroxylation of aromatic rings (Kitano, 1992; Kunai, 1988) to phenols and the direct dihydroxylation of olefins (Myers, 1987) with oxygen appear promising, although substantial advances in catalytic technology are required. The contrasts between the current multistep processes and the potential one-step technologies are dramatic:

Phenol Manufacture

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Cur : Benzene + propylene -> cumene Cumene -> cumene hydroperoxide -> pheno! + acetone Potential: Benzene + dioxygen -> pheno! + energy

Propylene Glycol Manufacture

Current: Isobutane \rightarrow tert-butyl hydroperoxide (TBHP) Propylene + TBHP \rightarrow Propylene oxide \rightarrow Propylene glycol Potential: Propylene + dioxygen + water \rightarrow Propylene glycol

Oxidative Dehydrogenation — Although the development of simple one-step functionalization processes like those described in the preceding paragraphs can have wide commercial application, it will always be necessary to generate olefins from aliphatic feedstocks. Olefins and arenes are among the most versatile classes of intermediates for making organic chemicals. Catalytic dehydrogenation is the current technology for conversion of paraffins to olefins, but it presents many challenges, 'especially for the less reactive lower alkanes. These dehydrogenations are highly endothermic and require that large quantities of heat be added to the reactors at very high temperatures. Equilibrium conversions are not high, and the elevated temperatures reduce selectivity. Loss of catalyst activity and coking are also significant problems.

Unlike simple dehydrogenation, oxidative dehydrogenation is not thermodynamically limited, because the reaction is driven to completion by oxygen as a hydrogen acceptor. Oxidative dehydrogenation is exothermic and, therefore, does not require the provision of large quantities of external heat to the reactor. The heat released in the reaction, along with the presence of oxygen, reduces coking. The oxidative dehydrogenation of butane to n-butenes has recently

been applied industrially, and attempts are under way to extend this technology to propane. Much more research is required, however, before oxidative dehydrogenation can be applied or a large scale to a wide variety of light aliphatic feedstocks. Active, selective catalysts that can operate under practical industrial conditions could provide breakthrough advances in light olefin manufacture. A special case with attractive potential is dehydrogenative coupling of methane to ethylene (Fox, 1993; Pereira, 1993).

Energy Froduction from Commercial Oxidation Reactions — Oxygenates make up most of the commodity chemical monomers that are produced from hydrocarbon feedstocks. Of the twenty largest volume monomers that contain elements other than carbon and hydrogen, sixteen contain only oxygen as the hetero element. Whenever a hydrocarbon and oxygen react, energy is produced, as in the industrial process chemistry shown in Figure 3.



Figure 3. Current Production of Oxygenates via Oxygen.

The energy produced in these reactions is very significant. Oxygen is an inexpensive oxidant but is difficult to control for selectivity because many of its reactions proceed by nonselective free radical processes. Industrial oxidation processes often use several steps to accomplish what could be done in a single step if a suitable selective catalyst was available, as illustrated in the examples above. Such single step processes could not only lower feedstock costs but could also supply the energy needs of a whole process and, in some instances, make the oxidation process a net exporter of energy.

6.2.1.3 Other Functionalizations of Hydrocarbons

In addition to the oxidations enumerated above, there are other ways to introduce functional groups into hydrocarbons that can have substantial economic and environmental benefits. Most are oxidative in character and can benefit from new developments in oxidation catalysis. The knowledge bases developed by studying reaction mechanisms and catalyst structures for oxidations should support innovation in catalyst development for direct functionalizations of the types described below.

One class of chemistry that is ripe for innovation in the short term is the introduction of fluorine substituents without the intermediacy of organochlorine compounds. There is a strong incentive to reduce the production and handling of organic chlorine compounds because of their environmental impact (Hileman, 1993), both in destruction of stratospheric ozone and in pollution of groundwater. At present, nearly all production of aliphatic fluorine compounds involves chloro compounds as intermediates. For example, most of the hydrofluorocarbons (HFCs) being developed as replacements for the ozone-destroying CFCs are made from chlorinated ethylenes. The leading refrigerant candidate, HFC-134a (1,1,1,2-trifluoroethane), is made from tri- or tetrachloroethylenes in multistep processes:

$$Cl_2C = CHCl + HF \rightarrow F_3CCH_2Cl \rightarrow F_3CCH_2F + HCl$$

 H_2
 $Cl_2C = CCl_2 + HF \rightarrow F_3CCFCl_2 \rightarrow F_3CCH_2F + HCl$

These processes are effective in producing the desired compounds, but are inefficient in that they produce huge quantities of HCl that must be recycled or neutralized. In addition, they require the production and handling of large quantities of chloroolefins.

A much more desirable approach to the manufacture of HFCs and fluoroolefin monomers would be based on the direct oxidative fluorination of hydrocarbons. This chemistry is illustrated by the oxidative fluorination of ethylene to vinyl fluoride:

$$H_2C = CH_2 + HF + O_2 \rightarrow H_2C = CHF + H_2O$$

This sort of reaction would closely parallel the oxidative chlorination of ethylene to vinyl chloride and the oxidative acetoxylation reaction used to manufacture vinyl acetate monomer. The current catalytic technologies for these latter processes would provide starting points for exploration of oxidative fluorination.

The replacement of organochlorine intermediates can be an important general topic in catalysis, going far beyond the interest in improved fluorocarbon syntheses. For example, many aromatic isocyanates are made by the reaction of aromatic amines with phosgene. Extensive work on the reactions of aromatic nitro compound's with CO indicates that it may be desirable to prepare aromatic isocyanates with these ingredients if the current catalysts can be improved (Parshall,

1992). Similarly, aliphatic isocyanates can be prepared by dehydrogenation of alkylformamides. In both cases, replacement of phosgenation by a CO-based process eliminates the hazards of handling phosgene and the environmental consequences of using organochlorine chemistry. Many other processes using organochlorine intermediates can be replaced by selective oxidation reactions like those described above. A prototypical example would be the direct oxidation of benzene to phenol. This reaction would replace the high temperature alkaline hydrolysis of chlorobenzene used by some phenol manufacturers.

Another class of reactions that will benefit greatly from innovations and improvements in heterogeneous catalysis is the introduction of nitrogen functionality into organic molecules. Nitrogen-containing compounds such as acrylonitrile, caprolactam, hexaroethylenediamine, and arene diisocyanates are essential monomers for major polymers such as acrylics, nylons, and polyurethanes. In addition, simple amines such as aniline and dimethylamine are intermediates for a wide range of organic products including pharmaceuticals, crop protection chemicals, dyes, and pigments.

Most approaches to organic nitrogen compounds are very indirect. For example, aniline is made by a sequence of energy-consuming reductions and oxidations. First, N_2 is reduced to ammonia, then the ammonia is oxidized to nitric acid, which is used to nitrate benzene to nitrobenzene that, in turn, is reduced to aniline. Simplification of this sequence could greatly reduce the energy consumption involved in hydrogen generation and in repeated purifications of intermediates. One potential innovation would be the direct oxidative amination of benzene to aniline:

$$C_6H_6 + NH_3 + O_2 \rightarrow C_6H_5NH_2 + H_2O$$

Development of catalysts for this kind of reaction could build on the catalysts for direct hydroxylation of benzene (Kitano, 1992; Kunai, 1988), mentioned earlier.

Nitriles derived from HCN are major building blocks for many important amines and carboxylic acids, for example:

HCN + Butadiene -> Adiponitrile -> 1,6-Hexanediamine

HCN +HCHO + NH₃ \rightarrow [(NCCH₂)₂NCH₂]₂ \rightarrow EDTA

Currently, HCN manufacture is carried out by the Andrussow process in which methane and ammonia are reacted over a precious metal catalyst at very high temperatures, at which HCN is the most thermodynamically favored product. A potentially significant advance would be the co-oxidation of ammonia and methane with a catalyst that would provide high yields even at moderate temperatures. Such a process would be closely analogous to the propane-based synthesis of a rylonitrile mentioned in Section 8.2.1.2 (Centi, 1992). Development of such processes for ammoxidation of alkanes would save energy and improve the economics for production of a range of nitriles and products derived from them. Another major nitrogen-containing monomer is caprolactam, the building block for nylon-6 (Tables 1 and 2). It is made conventionally by an acid-promoted Beckman rearrangement of cyclohexanone oxime, in which the oxime unit is isomerized to an amide function:

$C=N-OH \rightarrow C(O)NH.$

Because a stoichiometric amount of sulfuric acid is used to bring about the isomerization, large volumes of dilute acid must be neutralized on completion. The low value coproduct, ammonium sulfate, must be dealt with. Development of a solid acid that would function as a true catalyst for the oxime rearrangement would be a major advance in this technology (Cusumano, 1992). The acid catalyst would have the same potential to improve the technology for manufacture of methacrylic acid and its esters. Currently, acetone cyanohydrin is hydrolyzed and dehydrated to form methacrylic acid with strong sulfuric acid. The reaction produces large volumes of dilute sulfuric acid containing ammonium sulfate. A catalytic solid acid might eliminate the dilution aspect as well as permit the recovery of ammonia from hydrolysis of the cyanohydrin. Developments in solid acid catalysis based on aluminosilicates and aluminophosphates could lead to major energy savings and reduced by-product formation (with concomitant environmental benefits) in both the caprolactam and methacrylate processes. Work on catalysts for these processes can build on research on solid acid catalysts for petroleum refining (Chapters 1 and 9).

A potentially valuable addition to the catalytic syntheses of polymer intermediates would be the development of catalytic chemistry to add ammonia or water to primary olefins or dienes in anti-Markovnikov fashion (*i.e.*, with the NH_2 or OH substituent on the terminal carbon of the olefin or diene). Success in the addition of ammonia to 1,5-hexadiene would provide one of the best possible syntheses of 1,5-hexanediamine, key ingredient in nylon manufacture. If would avoid the need to make and hydrogenate adiponitrile, which is produced using HCN or acrylonitrile, both of which are made by high temperature processes involving large inputs of hydrocarbon or energy. A closely analogous objective would be the anti-Markovnikov addition of water to primary olefins to give primary alcohols, many of which are made by hydroformylat²on/ hydrogenation today. A special case with large economic value would be the selective addition of water to butadiene to form 1,4-butanediol or tetrahydrofuran. Success in this reaction would replace the relatively unselective oxidations of butane or benzene currently employed.

The difficulties in attempting to catalyze the selective addition of water or ammonia to olefins should not be underestimated. The reactions are only marginally feasible from a thermodynamic viewpoint - conversions of less than 10% can be expected at 100° C. The equilibrium becomes much less favorable above 100° and is only modestly affected by increase of pressure. Normal acid catalysis gives almost exclusively the unwanted Markovnikov isomer with the NH₂ or OH substituent on a secondary carbon.

From the viewpoint of trying to develop catalysts for these useful addition reactions, industrial homogeneous catalysis can provide many helpful conceptual inputs. Coordination of an olefin to a cationic metal complex facilitates the addition of a nucleophile such as ammonia or water and may "steer" the substituent to the desired carbon (Knoth, 1975). Oxidative addition of the

N-H bond of ammonia to a low valent transition metal complex can give a hydrido metal amide that, under some conditions, can add the N-H bond across the C=C bond of an olefin (Casalnuovo, 1988). It is also known that radical mechanisms for the addition process (e.g., HBr plus a radical initiator) can give the desired anti-Markovnikov additions to olefins. Concepts such as these, borrowed from homogeneous catalysis, can provide the basis for exploration of heterogeneous catalysts for olefin additions. Indeed, a good starting point for such studies may be "anchoring" homogeneous catalysts to solid support materials.

Given the mechanistic information available from homogeneous catalysis of addition reactions, these reactions may be good candidates to test the design of new catalytic materials. This topic may be a fertile field for collaboration between industrial scientists and their colleagues in the national laboratories and the DOE-supported university programs. Past industrial research in the area has been largely empirical, but the government and academic groups could bring many strengths in fundamental chemistry that would be needed for catalyst innovation.

6.2.2 New Feedstocks

The preceding sections have dealt primarily with processes to use hydrocarbon feedstocks more efficiently. These feedstocks derive principally from petroleum and natural gas, which are likely to be the dominant feedstocks for the chemical industry for the next 20-30 years. Because these carbon sources will become scarcer and more expensive, we must also look to alternative feedstocks that will be available for the indefinite future. Some obvious sources are coal, shale oil, and tar sands that are abundant in North America, although they suffer disadvantages in terms of being more difficult to process than the current feedstocks. Eventually, however, even these resources are likely to be exhausted or, at least, difficult to utilize economically.

Plant-derived materials, both oils and cellulosics such as corncobs, wood chips and bagasse (sugar cane residues), constitute carbon-containing feedstocks that are renewable by photosynthesis. These materials are referred to as biomass. Other forms of biomass that seem inexhaustible in the sense that they are produced constantly are the eliganic by-products of modern society like garbage, paper and plastic trash, and sewage sludge. Waste materials, both the cellulosics and those of human origin, are particularly attractive to consider as feedstocks because they are cheap and widely available. The cost, apart from collection and transportation, is essentially equivalent to their fuel value if t^{1} -wy were to be burned in a boiler or incinerator to recover their energy content as heat or electricity. The collection and transportation costs cannot be overlooked, however, because the sources such as farms and households are scattered, and collection systems are not always well developed. Another complication is thet waste products such as garbage, trash, and sewage are heterogeneous materials. Sorting and preprocessing may be uneconomical as is often observed in recycling operations.

For economical processing of heterogeneous wastes, generic processes are required to obviate the need to sort the mixtures. Those available in the near term generally do not involve heterogeneous catalysis. Some examples are the collection of methane-rich gases from landfills and the acid-catalyzed hydrolysis of cellulosic wastes. The methane collection approach to produce a useful feedstock is being tested in a small facility near Denver in which landfillgenerated gases are converted to syngas which, in turn, is converted to diesel fuel (Mills, 1993). In the longer term, it may be more attractive to convert solid organic wastes to syngas directly by high severity reforming processes like those used for the gasification of lignite. The syngas produced from biomass (or coal or shale oil) by reforming is a versatile feedstock for the manufacture of fuels (Chapter 9) and chemicals. As discussed below, innovations in catalytic technology for the use of syngas can have a major impact on the production of industrial chemicals and polymer intermediates.

Another way to use biomass as a renewable feedstock is to produce crops specifically for chemical production. One historical example is the production of palm, cottonseed, and other vegetable oils as intermediates for the manufacture of soaps, detergents, and margarine. Another is the growth of gain and sugar cane for production of ethanol to be used as a fuel and as a chemical intermediate. In this example, the primary processing technology is fermentation. With both vegetable oils and fermentation ethanol, however, subsequent processing steps commonly involve catalytic reactions such as hydrolysis, hydrogenation, or oxidation. The catalysis of these specific reactions is well developed and does not seem appropriate for major research support.

6.2.2.1 Catalytic Processes Using Syngas

Synthesis gas (syngas), a mixture of carbon monoxide and hydrogen, is now produced from various carbon sources including methane and coal. As mentioned above, it can also be made from many abundant forms of biomass. Many current industrial processes use syngas as a basic building block for manufacture of commodity chemicais (Figure 4). All are highly optimized and very efficient. These processes, apart from methanol synthesis, utilize soluble catalysts.





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The usage of homogeneous catalysts reflects the fact that carbon monoxide reacts with most transition metals to give soluble or volatile metal carbonyl derivatives. It has been extremely difficult to "anchor" catalytic complexes to a support so that the catalytic metal is not leached from the support during extended reaction periods. The "anchoring" of catalytic molecular complexes to insoluble supports is a major challenge in design of heterogeneous catalysts for reactions involving CO as a reactant.

Syngas, whether derived from fossil or renewable feedstocks, is an extremely versatile source of chemicals. Major industrial chemicals such as methanol, formaldehyde, and acetic acid derivatives are currently made in one or two steps from syngas. Potential catalyst improvements for methanol synthesis could make these processes even more attractive. Other potential industrial processes simply await improvements or inventions in syngas conversion. Figure 5 shows an array of oxygenated products that can, in principle, be made solely from syngas in reactions that have been demonstrated in the laboratory, but have not been commercialized on a significant scale. Some examples are production of ethanol and acetaldehyde by homologation of methanol and synthesis of ethylidene diacetate for conversion to vinyl acetate. Direct synthesis of ethylene glycol from syngas would have a substantial economic and energy conservation impact (Pruett, 1977). In all these cases, improvements in catalyst properties could lead to use in new economical, energy-conserving processes. In these reactions, as in the oxidative carboxylation processes discussed below, develowment of heterogeneous catalysts may be essential to provide catalysts with the chemical and physical properties needed for industrial application. Success would open the way to use of abundant or renewable feedstocks for production of some of the largest-scale chemical products made today.



Figure 5. Potential Product Network Based on Syngas.

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6.2.2.2. Oxidative Reactions of Syngas-Based CO

Although most commercial technology utilizing syngas is reductive in nature, there are large opportunities for new chemistry based on oxidation of CO (Figure 6). Most of these opportunities are apt to involve multifunctional heterogeneous catalysts, somewhat analogous to the multifunctional catalysts for oxidation of hydrocarbons discussed earlier in this chapter. In fact, many of the oxidative processes for CO are likely to incorporate similar metal oxides as co-catalysts or catalysts supports.



Figure 6. Potential Commercial Processes Based on Syngas.

The oxidative reactions of CO and alcohols to give dialkyl oxalates and carbonates, as shown in Figure 6, are currently practiced commercially (Parshall, 1992). Ube Industries carvies out the reaction of CO with 1-butanol and 1-butyl nitrite (as an oxidizing agent) in the presence of a palladium catalyst to give primarily dibutyl oxalate along with small amounts of dibutyl carbonate. Dialkyl carbonates can be made the major products with copper catalysts. Dimethyl carbonate, a substitute for the highly toxic phosgene in many reactions, is produced this way by Enichem. Both of these syntheses may be carried out with either homogeneous or heterogeneous catalysts. Most of the chemistry in Figure 6 has been demonstrated with soluble catalysts, but it seems likely that practical applications will depend on the development of multifunctional beterogeneous catalysts. The heterogeneous catalysts should reduce the corrosion problems that are associated with palladium chloride-based liquid phase systems and should simplify product separation from catalysts. Newly designed catalyst systems can sequentially coordinate and assemble mixtures of reactants like those shown in Figure 6 (Lyons, 1991). Advanced catalyst design makes it possible to control the numbers and positions of the CO entities that will be oxidatively added to a hydrocarbon substrate. The practical challenge is synthesis of long-lived, active, selective catalyst species on the surfaces of useful supports. The supports may play a co-catalytic role in activating dioxygen or some other practical oxidant needed for a truly catalytic process.

Both for conventional syngas reactions and for promising new oxidative reactions of CO, we need better understanding of the interactions of CO with solid surfaces. Despite decades of work on the mechanism of the Fischer-Trepsch reaction (Hindermann, 1993) and on CO binding to metals, the sheer complexity of these processes prevents design of new catalyst systems. The challenge is especially great in oxidative carboxylations because exploration of these reactions has been "muted and because two different kinds of catalysis (CO activation and oxidant generation) must interact constructively (Hsu, 1986; Lyons and Hsu, 1987). Fortunately, knowledge gained from studies of hydrocarbon oxidation catalysis should apply to oxidative carboxylation catalysis. The metal oxide catalysts discussed for C-H activation may be useful as active supports for metallic CO activation sites. A wide variety of organometallic species on metal oxide supports have been characterized (Zecchina, 1993), bir this field of research seems very promising for enhanced understanding of syngas catalysis.

6.3 POLYMERS

As noted in Table 2, many of the largest scale polymers are produced by catalytic processes. Polyolefins are commonly made using supported organometallic catalysts related to the Ziegler-Natta catalysts first developed for such processes, but are far more efficient than the originals. Successive generations of olefin polymerization catalysts have improved in efficiency to the point that they no longer need to be removed from the finished product. Ingenious engineering has led to gas phase processes that rain out polymer pellets nucleated on individual catalyst grains. With the latest "single-site" catalysts being based on metal oxide-supported metallocene complexes, excellent control of molecular weight and tacticity is obtained. In many ways, the development of the olefin polymerization catalysts is a model of intelligent catalyst design based on mechanistic understanding, characterization of catalyst-support interactions, and understanding of process engineering requirements (Burdett, 1992).

Despite the economic value of polymers to the U. S. economy (about \$25 billion per year for the polymers in Table 2), research on polymerization catalysts is probably a low priority for the U. S. Department of Energy Some factors in this conclusion are:

- The opportunities for energy and feedstock savings are small because polymerization processes commonly proceed in high conversion and nearly quantitative yield. There are, however, significant opportunities for energy and feedstock conservation in the manufacture of polymer intermediates, as discussed in Section 6.2.
- The environmental impact of the polymerization catalysts themselves is small, especially as chromium-based ethylene polymerization catalysts are replaced by new,

environmentally innocuous catalysts. There is still a desire to replace antimony catalysts used in the manufacture of polyesters, but this problem is being addressed by the chemical industry.

▶

The potential contribution to the competitiveness of U S. industry is also small because the current processes are so efficient and because many U.S. firms continue to enhance this technology.

The major areas in which research could assist U. S. polymer producers lie in improved process technology for polymer intermediates (Section 2) and in characterization of metal oxide surfaces that may be used as catalyst supports. Many of the characterization issues discussed in Chapter 3 are just as relevant to polymerization catalysts as to the catalysts used in petroleum refining. Fundamental information leading to the understanding of surface paenomena on "real catalysts" could be valuable. Researchers in surface characterization should be aiert to the implications for polymerization catalysis. In a complementary sense, knowledge of the chemistry of supported organometallic polymerization catalysts should be transferable to the design of catalysts for many other applications.

6.4 SUMMARY OF RESEARCH NEEDS

The catalytic developments that can have the greatest impact on production of industrial chemicals fall into two major categories:

- Selective oxidation and functionalization of hydrocarbons. Because the feedstocks for these processes are largely petroleum and natural gas, this objective is short-term in the sense of benefiting the chemical and petroleum industries in the next 20 to 30 years.
- Heterogeneous catalysis for reactions based on synthesis gas. These catalyst developments are longer-term because they use a feedstock that can be derived from abundant or renewable carbon sources, such as coal and biomass. However, success in this area can also have near-term impact because synthesis gas is currently available from petroleum and natural gas. Major opportunities exist in the development of chemistry and technology for oxidative carboxylation reactions.

The potential energy/feedstock impact of success in these two areas can be estimated. Success in the targets identified for selective oxidation catalysis may lead to savings of about 8.5 million barrels of petroleum and natural gas liquids per year. This amount is about one percent of the annual total petroleum used for chemical feedstocks or about half as much petroleum as the U.S. consumes in one day for all purposes. While the chemical feeds ock savings are small compared to those attainable in the fuels area, the economic impact would be substantial. [Basis for the estimate: The oxygen-containing chemicals in Table 1 consume about 50 billion ppy. of hydrocarbon feedstocks. An average 5% yield increase in each of their manufacturing processes would save 2.5 billion ppy. of petroleum and natural gas. Some processes, such as the oxidations of butane and cyclohexane, might afford 10% yield increases. Others, like the

oxidation of p-xylene to terephthalic acid, are unlikely to give yield increases above 2%. A 5% average seems plausible.]

In contrast to the modest feedstock savings realistically expected from improved catalysts for hydrocarbon oxidation, larger but more speculative savings may be forecast for catalyst developments in the use of syngas or bio-derived feedstocks. It may be reasonable to set a goal of annually shifting 1% of the chemical industry's feedstock needs from petroleum to syngas or renewable feedstocks. Substituting abundant or renewable raw materials for an additional 8.5 million barrels of petroleum each year would have a large cumulative effect. Over the course of four decades (a reasonable transition period for such a large and varied industry), the feedstock savings would rise to about 5% of total U.S. petroleum consumption.

The research required in both areas centers on better understanding of metal oxides, both as oxidation catalysts in themselves and as supports for metals. Catalyst-support interactions may be critical in the metallic catalysts.

6.4.1 Selective Cridation and Functionalization Catalysts

We recommend that highest priority be given to the synthesis, characterization, and catalytic evaluation of catalysts for the selective oxidation of hydrocarbons, especially alkanes, with air or oxygen. In particular, greater understanding is required in the catalytic functions that lead to activation of dioxygen and of hydrocarbons.

Selective oxidation catalysis can yield major savings in energy and feedstocks, both through improvements in existing processes such as the oxidation of butane to butadiene or maleic anhydride, and through invention of new processes to convert hydrocarbons to functionalized organic compounds. Many current hydrocarbon oxidations operate by free radical mechanisms that are relatively unselective. We know, however, that metalloenzymes and analogous homogeneous catalysts can attain high selectivities by generation of unique oxidants such as M = O species, and through controlled binding of the hydrocarbon substrate. Similarly, there is a large body of empirical knowledge about existing catalysts that can be used to develop new catalysts if the necessary scientific foundation can be developed. For example, the catalysts developed by Sohio for the animoxidation of propylene to acrylonitrile are basically bismuth molybdates, but the optimum commercial catalyst contains traces of many other metal ions that contribute to its stability and selectivity. Understanding the role of these additives could go far toward intelligent design of new catalysts. Interestingly, the catalysts as for oxide-supported metal oxide catalysts as for oxide-supported metals (Owens, 1993).

Integrating insights from diverse sources with new information from structural and computational studies of metal oxides can yield major benefits in the development of new, environmentally friendly processes that will conserve energy and feedstocks. Some examples of replacing complex, multistep processes are the following:

Methane $+ O_2 \rightarrow$ inethanol

Benzene + $O_2 \rightarrow$ phenol

Ethylene + O_2 + HF \rightarrow CH₂=CHF \rightarrow CH₃CHF₂ HFC-152a

[HFC-152a is an attractive replacement for ozone-depleting CFC's in applications including refrigeration and air conditioning.]

6.4.2 Catalysts for Synthesis Gas Reactions

We recommend exploration of heterogeneous catalysts for reactions of carbon monoxide, especially the relatively undeveloped oxidative carboxylation reactions.

Syngas (CO and H_2 in varying proportions) can be produced from a wide variety of carbon sources and is now used extensively in manufacture of major industrial chemicals such as methanol, scetic acid, and the oxo alcohols. Broadening the process applications of syngas to a wider range of organic chemicals could lead to a "syngas economy" for the chemical and petrochemical industries. Developing the catalytic technology for a syngas economy would ease the transition from petroleum and natural gas feedstocks to abundant and renewable feedstocks, because the "downstream" process technology would be the same once the syngas is generated. In the conversion of syngas, it is preferable to produce oxygenated fuels/chemicals with a value exceeding that of the corresponding hydrocarbon products. This strategy increases overall thermal efficiency and provides producis specifically responsive to future needs for high efficiency and environmental concern.

Development of heterogeneous catalysts for CO reactions is a critical step in the transition to the syngas technology. Most current CO-based processes, apart from methanol synthesis and the Fischer-Tropsch technology, employ homogeneous catalysts. These soluble catalysts have many virtues, but difficulties in separating the catalysts from product mixtures limit the range of products to which they can be applied. Development of heterogeneous catalysts, which have many advantages in terms of process engineering, would facilitate the conversion to syngas as a feedstock. Because of the remarkable ability of CO to convert transition metals to soluble or volatile species, the "anchoring" of catalytic species to supporting materials presents special challenges as well as significant opportunities. Fortunately, the base of mechanistic information on heterogeneous catalysts for CO reactions is growing rapidly (Hindermann, 1993).

Oxidative carboxylation reactions, in particular, offer opportuniti. for innovative new processes that would conserve energy and feedstocks. For example, the oxidative carboxylation of alkanes to esters would provide new classes of economical and efficient oxygenates for fuels.

REFERENCES

Ai, M. 1992. Catalysis Today 13:679.

Burdett, I. D. 1992. The UNI OL Process. Chemtech. 22(10) (Oct.):616-23.

Casalnuovo, A. L., J. C. Calabrese, and D. Milstein. 1988. Rational Design in Homogeneous Catalysis. J. Am. Chem. Soc. 110:6738-44.

Centi, C., ed. 1993. Catalysis Today. 16(Jan.):1.

Centi, G., R. Grasselli, and F. Trifiro. 1992. Catalysis Today 13:661.

Cusumano, J. A. 1992. New Technology and the Environment. Chemzech. 22 (Aug.):482-89.

Fox, J. M. 1993. The Different Catalytic Routes for Methane Valorization: An Assessment of Processes for Liquid Fuels. Catal. Rev.-Sci. Eng. 35(2):169-212.

Gellings, P. J. and H. J. M. Bouwmeester. 1992. Catalysis Today 12:1-105.

Hileman, B. 1993. Concerns Breaden over Chlorine and Chlorinated Hydrocarbons. Chem. Eng. News. 71 (19 Apr.):11-20.

Hindermann, J. P., G. J. Ilutchings, and A. Kienemann. 1993. Mechanistic Aspects of the Formation of Hydrocarbons and Alcohols from CO Hydrogenation. Catal. Rev. - Sci. Eng. 35(1):1-127.

Hsu, C. Y., U.S. Patents, 4,855,485 (1989); 4,827,023 (1989); 4,737,591 (1988); 4,620,027 (1986).

Kennedy, M., A. Sexton, B. Kartheuser, E. MacGiollacoda, J. B. McMonagle, and B. K. Hodnett. 1992. Selective Oxidation of Methane to Formaldehyde. *Catalysis Today*. 13:447-454.

Kitano, T., T. Wani, T. Ohnishi, J. Li-Feu, Y. Kuroda, A. Kunai, and K. Sasaki. 1992. Gas Phase Oxidation of Benzene to Phenol Using Pd-Cu Composite Catalysts. Catalysts Letters. 11(1):11.

Knoth, W. H. 1975. Reactions of Ethylene Coordinated to Metals. Inorg. Chem. 14:1566-72.

Kunai, A., K. Ishihata, S. Ito, and K. Sasaki. 1988. Heterogeneous Catalysts for Continuous Oxidation of Benzene to Phenois. Chem. Lett. 12:1967-1970.

Kuroda, T. and M. Okita. 1992. Japanese Patents JP04128247, JP04059739, JP04059738.

Lyons, J., P. Ellis, and V. Durante. 1991. Studies in Surf. Sci. and Catalysis, 67:99.

Lyons, J. E., C. Y. Hsu. 1987. Proceedings of Catalytica's Fourth Annual Science and Technology Sciencinar, Advances in Catalysis, pp. 151-181, Oct 25-27.

Mills, G. A. Oct. 1993. Status and Future Opportunities for Conversion of Synthesis Gas to Liquid Energy Fuels. DOE report. NREL/TP-412-5150, NTIS # DE93010025.

Myers, R., R. Michaelson, and R. Austin. 1987. *Petroleum Division Preprints*. Amer. Chem. Soc., vol. 32, p.1. Washington.; U. S. patents 4496778 and 4496779. Austin, R.G., and R. C. Michaelson, U. S. Patent 4,390,739 (1983).

Owens, L. and H. H. Kung. J. Catal., in press.

Parshall, G. W. and S. D. Ittel. 1992. Homogeneous Catalysis. New York: Wiley.

Pereira, P. et al. 1990. The Conversion of Methane to Ethylene and Ethane with Near Total Selectivity by Low Temperature Oxydehydrogenation. Catal. Letters. 6:255-63.

Periana, R. et al. 1993 Science. 259.

Pruett, R. 1997. Annals New York Acad. Sci. 295:239.

Stadig, W. 1992. Chem. Proc. (Aug.) p. 28.

Zecchina, A. and C. Otero Arean. 1993. Structure and Reactivity of Surface Species Obtained by Interaction of Organometallic Compounds with Oxidic Surfaces: IR Studies. *Catal. Rev.-Sci. Eng.* 35(2):261-317.