Chapter 9

CATALYSTS FOR LIQUID TRANSPORTATION FUELS FROM PETROLEUM, COAL, RESIDUAL OIL, AND BIOMASS

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9.1 INTRODUCTION

Heterogeneous catalysis has played a major role in production of our liquid fuels supply. This role has increased dramatically since the ordinary distillation processes, first used to produce liquid fuels, were not adequate for producing the quantity and quality of liquid fuels necessary for the "hydrocarbon economy". In fact, catalytic cracking, reforming, and hydrotreating processes were largely responsible both for the availability of large quantities of motor fuels and for the growth of the large research effort in heterogeneous catalysis which occurred after W.W. II. It is the purpose of this section to outline future challenges in liquid fuels production. Economic scenarios have been described (Longwell, 1990). We will also describe opportunities in heterogeneous catalysis research which will enable us to meet these challenges. We should also recognize that heterogeneous catalysis plays a major role in the development of better catalytic converters which have had and will continue to have a major impact on emissions from liquid fuel burning engines. This topic has been covered in a previous chapter.

9.2 FUELS FROM PETROLEUM FEED STOCKS

In the past thirty years efficiency and environmental factors have been the drivers in the refining of petroleum to liquid transportation fuels. Generally, there has been a trend to use more of the petroleum barrel for liquid transportation fuels. This involves catalytic cracking, using zeolite catalysts for breaking down larger molecules to motor fuels boiling range, naphtha reforming, using noble metal catalysts to reform smaller molecules into this range and hydrotreating, using sulfide catalysts to remove sulfur and nitrogen. The past has seen remarkable progress in the science and technology. However, there is still room for improvement, and progress is needed to meet the environmental demands placed on the catalysts. In most cases fundamentals of catalyst structure/function are still needed.

9.2.1 Environmental Drivers

Generally, the impact of the 1990 Amendments to the Clean Air Act on catalysts and catalytic processes will be to demand more from existing processes in the short run, and new catalysts and catalytic processes in the long run. Catalysts will be required th[illegible] [illegible]les in the proper motor fuels boiling range more efficiently with less aro[illegible] [illegible]anched paraffins. Catalytic cracking processes are currently at 70% effic[illegible] further improvements could lead to dramatic results. A 1% improvement leads to a 22[illegible] bbl/year savings (Longwell, 1990). Catalysts will also be required which saturate aromatics and remove sulfur more effectively. Since oxygen addition is now mandated, better catalysts will be required to produce oxygenates like MTBE, particularly the isobutylene needed for MTBE manufacture.

9.2.2 Improvements to Existing Catalysts

The following sections list studies in understanding and performance which will be necessary for the current generation of catalysts to meet demands for further improvements in efficiency and environmental performance. Three major classes of existing catalysts are considered: zeolites, sulfides, and noble metals.

9.2.2.1 Zeolites

Zeolites are an example of a class of catalytic materials where structure/function relationships have a firm foundation because of detailed knowledge of the structure and its effect on reaction activity and selectivity. It is also a class of catalytic materials which has proved remarkably successful and important in petroleum refining technology.

Zeolites also continue to present the promise of new and important innovations. We have not yet reached the limit of the potential of this class of catalytic materials. New structures are being discovered regularly and the catalytic potential of the zeolitic structures, such as VOPO and others, are still being investigated. Still, more work needs to be done to understand the complex structural relations which can exist among zeolitic phases and how they effect catalyst preparation and function. Preparative methods for controlling phases and particle sizes are still needed. New zeolites are constantly demanded for new applications, such as producing more olefins as precursors for oxygenate production. Following is a list of research needs in this area:

- Structure/catalytic function relations for existing zeolites and environmentally important fuels reactions. Particularly important is to build on the understanding of acidity in these catalysts.
- A better understanding of zeolite structure and phase relationships as provided by advanced probes and theory.
- A better understanding and control of zeolite synthesis and catalyst preparation.
- The discovery of new zeolitic materials and their relation to catalytic reactions of interest.
- Development of zeolitic materials for reactions specific to environmental fuels issues. For example, zeolites for producing isomerized olefins as precursors for MTBE.

9.2.2.2 Sulfide Catalysts

Sulfide catalysts are probably the oldest class of catalytic materials used in the production of liquid transportation fuels. Developed after W.W.I for the hydrogenation of coal tar liquids, the sulfide catalysts are currently used in virtually every refinery in the world. They are used to remove sulfur, nitrogen, and to hydrogenate feeds. They may be used before another catalytic process, such as reforming or catalytic cracking, to hydrogenate and to remove sulfur which may poison the noble metal or zeolitic catalyst. Catalytic cracking feedstock hydrotreating is an example. Or they may be used after catalytic treatment to finish the product and meet final product specification. When used in this form they are called hydrotreating catalysts.

Modern sulfide catalysts are usually alumina supported Mo or W based catalysts which are promoted with Co, Ni, or both. This promotional effect is one of the most interesting and useful of catalytic phenomena. It has also been the subject of intense investigation. However, though some progress has been made, it still remains something of a mystery, especially regarding the structural details of the effect. The electronic nature of the promotional effect has been established on theoretical grounds (Harris, 1988). It is thought that a special phase exists which contains the promoted sites, and this has been termed the CoMoS phase (Candia, 1982). Also, recently the relation of the layered MoS_2 structure to hydrogenation activity and desulfurization activity has been demonstrated (Daage, 1993). Work in establishing the basis for activity and selectivity in these materials has been hindered because the working catalytic materials are highly disordered, and reliable characterization techniques for disordered materials are lacking.

The current generation of sulfide catalysts has proven remarkably successful in meeting past sulfur removal goals. Because these goals have been met in the past, these catalysts have not received as much attention as other catalysts. However, it is clear that the current generation of catalysts is not sufficient to meet the environmental demands placed on sulfur removal, nitrogen removal, and hydrogenation of aromatics. Improved catalysts are required which are based on a firm understanding of catalytic structure/function relations. Following is a list of research needs in this area:

- A continued effort to apply theoretical techniques to understanding the fundamental origins of catalytic phenomena in the transition metal sulfide catalytic materials.

- A continued development of an understanding of the promoted system with an ability to optimize activity or extrapolation to new catalytic systems.

- A continued development of structure/function relations in these systems with an emphasis on larger molecules which represent the most important barriers to new levels of sulfur removal. Thiophene studies should be de-emphasized.

- Development of an understanding and optimization of the sulfide's ability to catalyze aromatic hydrogenation in the presence of sulfur.

- Development of characterization techniques which can reliably characterize disordered sulfides. For example, further work must be done with the EXAFS technique to demonstrate its usefulness on disordered materials.

- Development of new catalytic processes which take advantage of the sulfide's ability to both desulfurize and saturate aromatics simultaneously.

9.2.2.3 Noble Metal Catalysts

Noble metal catalysts instituted a revolution in reforming technology when the Pt/alumina catalyst was first introduced by UOP in the early fifties (Haensel, 1991). This was a major innovation for catalytic sciences because many thought that a noble metal catalyst could not be economically introduced in refining technology. The original Pt/alumina catalysts were followed by improvements in selectivity and activity provided by the Pt/Ir/alumina and the Pt/Re/alumina catalysts in the seventies. These catalysts are in use today, and there is still room for further improvements.

The noble metal catalysts provided some of the best examples of basic and applied catalyst research in the recent past. The basic periodic trends for ethane hydrogenolysis and other reactions led the way toward an understanding of the role of noble metals in catalysis (Sinfelt, 1978). Detailed spectroscopic analyses of noble metal catalysts have given remarkable insight into their basic properties.

However, many problems remain to be understood and catalyst improvements need to be made. Following is a list of research areas in this field:

- An understanding of the basic structural chemistry of small noble metal clusters needs to be developed. Bimetallic clusters and the interfaces of noble metal particles in their catalytic state need to be advanced.

- Theoretical and structural probes need to be advanced which relate to the nobel metal catalysts in their highly dispersed states.

- Structure/function relations need to be developed which are related to small particles of noble metal catalysts for reactions of environmental importance.

- New noble metal catalysts need to be developed based on the fundamental principles outlined above. This may include an understanding of the role of 4 and 5d electrons and how noble metals may be replaced by cheaper metals.

- The role of carbonaceous overlayers needs to be elucidated and the learnings applied to develop new catalysts.

9.2.3 The Need for New Catalytic Materials

Most of the new catalytic materials required for liquid transportation fuels will be covered in sections below when alternate fuels processing will be discussed. This is because improvements to current hydrocarbon-based liquid fuels will be done with existing processing equipment, requiring a drop-in catalyst, whereas alternate fuels production will require new processes and equipment, making the application of new catalytic materials more favorable. However, there are some examples of new catalytic materials which can impact on the current hydrocarbon fuels picture.

9.2.3.1 Solid Acids

There is a need to replace current alkylation and isomerization processes which involve HF or H_2SO_4 with processes which are environmentally more acceptable. This may be done through the discovery of solid acids which have the appropriate acidity. The strongest superacids would be expected to be too strong for this application but acids with intermediate strengths may be discovered which effectively perform this reaction (Hsu, 1992). Research should be supported for theoretical understanding and development of new strong acid catalytic materials

9.2.3.2 Carbides

Transition metal carbide catalytic materials have been reported to mimic noble metals in activity. Their development has been hindered by the ability to synthesize carbides, as well characterized materials, with high surface area. Research should be performed which is directed to developing synthetic methods to achieve this and to demonstrate catalytic structure/function relationships. The work of Brewer-Engel (1968) in describing the thermodynamics of compound formation between early and late transition metals of the periodic table may be particularly useful here.

9.3 CONVERSION OF SYNTHESIS GAS TO LIQUID FUELS

9.3.1 Overview

The manufacture of liquid energy fuels from syngas (a mixture of H_2 and CO, usually containing CO_2) is of growing importance and of enormous potential (Haag *et al.*, 1987; Mills, 1993) because:

- Abundant U.S. supplies of coal, gas, and biomass can be used to provide the needed syngas.
- The liquid fuels produced, oxygenates or hydrocarbons, can help lessen environmental pollution. Indeed, oxygenates are required to a significant extent by the Clean Air Act Amendment of 1990.

- Such liquid synfuels make possible high engine efficiencies since they have high octane or cetane ratings.

- There is new, significantly improved technology for conversion of syngas to liquid fuels and there are promising opportunities for further improvements.

Much of the improved technology for selective synthesis of desired fuels from syngas has resulted from advances in catalytic chemistry. However, novel process engineering has been particularly important recently, utilizing known catalysts in new configurations, to create new catalytic processes.

The manufacture of liquid synfuels is capital intensive. Thus, in evaluating advances in fuels technology, focus is on potential for improved economics, particularly on lowering plant investment costs. A second important criteria is the potential for environmental benefits.

Improved technology and special needs, some political and some environmental, have led to a variety of recent commercial installations of liquid hydrocarbon fuels from syngas. The novel MTG (methanol-to-gasoline) process began operation in New Zealand in 1985 (Tabak and Yurchak, 1990; Mills, 1993). A new type of Fischer-Tropsch unit, a fixed fluid bed unit, was installed by SASOL in South Africa in 1989 (Dry, 1990). The largest synfuels plant is being started up in Mossel Bay, South Africa, using SASOL synthesis technology. Also in 1993, the SMDS (Shell Middle Distillate Synthesis) plant will begin operation in Malaysia. A small plant near Denver is in start-up operation producing diesel fuel based on slurry-phase catalytic conversion of syngas made from landfill gas.

Insofar as oxygenate fuels from syngas are concerned, gasoline blends containing mixed alcohols manufactured from syngas were marketed in Italy for a period of time in the 1980s. In the U.S., the Tennessee-Eastman plant has been recently expanded, manufacturing products which include methanol, using syngas made from coal. Blends of gasoline and low levels of methanol have been tested extensively. Higher molecular weight alcohols are usually included in the blend to help prevent phase separation which can occur when small amounts of water are inadvertently present. At present, blends containing low levels of methanol are not well regarded as commercially desirable by the public and industry.

In contrast, fuel M85, 85% methanol and 15% gasoline, provides excellent performance in vehicles designed for this fuel. M85 is being marketed in California and other U.S. locations. In addition, flexible fuel vehicles, FFVs, are being manufactured which can use gasoline or methanol or blends of any intermediate composition.

Methyl tertiary butyl ether, MTBE, was first introduced in gasoline blends in Italy in 1973. Its growth has been phenomenal (Haigwood, 1991), reaching 6 million gallons per day in the U.S. (gasoline is 300 mgpd). It is synthesized by the reaction

$$CH_3OH + \text{iso } C_4H_8 \rightarrow CH_3OC(CH_3)_3$$

MTBE is partly derived from syngas; 36% by weight of MTBE is provided by methanol. Plants to manufacture tertiary-amyl methyl ether, TAME, are also being installed.

One interesting technical innovation in ether synthesis is the use of "catalytic distillation" to carry out the above reaction with the advantage that the reaction is driven almost 100% to the ether.

There has been concern about insufficient isobutene for MTBE needs. However, the need is being met by dehydrogenation of isobutane and by new cracking catalysts which produce higher than usual amounts of isobutene. Isobutanol can be produced from syngas and dehydrated to isobutene.

The use of oxygenates in fuels is greatly influenced by the Clean Air Act Amendment (CAAA) of 19.0. In 44 cities it is required that gasoline contain 2.7% oxygen (equivalent to 15 vol.% MTBE) in the winter months, beginning in 1992. In these cities, the carbon monoxide in the air exceeds the amount deemed allowable for health reasons. Further, in 1995 gasoline in 9 cities not in compliance with air standards are to contain 2% oxygen year-round. There are other later requirements for clean fuel fleets. It should be noted that gasoline reformulation has been voluntarily instituted to a large degree by the petroleum industry. Reformulated gasoline contains some oxygenates.

Our discussion will be concerned with two types of hydrocarbon fuels and three types of oxygenate fuels which can be synthesized from syngas. Seven alternative reaction pathways are shown in Figure 1.

9.3.2 Chemistry of Syngas Catalysis

The development of improved catalysts and processes has, to a great degree, been made possible by advances in understanding the chemistry of syngas catalysis reactions (Herman, 1991).

Particularly important have been advanced instrumental characterization of catalyst surface structures, as well as reaction mechanism studies using isotopic labeling and kinetic research. It is now clearly established, perhaps unexpectedly, that over Cu-ZnO/Al_2O_3 catalysts and under industrial conditions for methanol synthesis, hydrogenation of CO_2 predominates over CO hydrogenation and that copper metal is the active catalytic component (Waugh, 1992). CO is converted to CO_2 by the water gas shift reaction. The reaction steps of the WGS reaction are independent of those in methanol synthesis. It is believed that methanol formation proceeds through reaction of CO_2 to formate and methoxy intermediates. It has been established that higher alcohol formation over alkali-containing catalysts is a kinetically controlled chain growth mechanism superimposed on a thermodynamic background. Experimental and theoretical calculations support the mechanism in which chain growth in oxygenate synthesis is *via* aldol addition with oxygen retention reversal (Klier *et al.*, 1992).

For hydrocarbon synthesis, a quantitative understanding has been developed of product carbon distribution numbers in Fischer-Tropsch synthesis over both iron- and cobalt-based catalysts

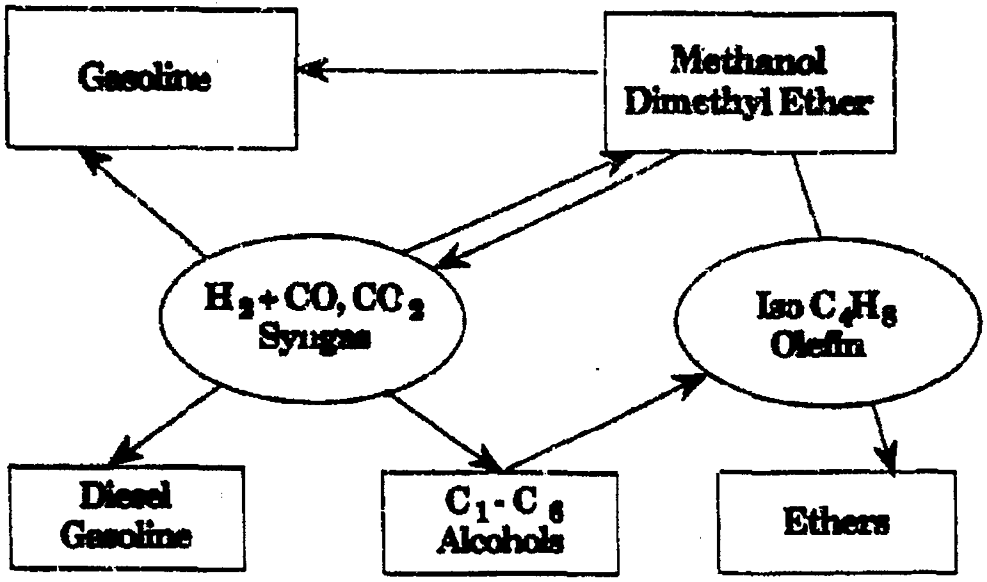

Figure 1. Pathways for Syntheses of Liquid Fuels from Syngas.

(Bartholomew, 1991). This knowledge, coupled with kinetic data, has been vital in the development of new processes for diesel and gasoline manufacture. Likewise, research on heat and mass transport are being used in critical development of greatly improved slurry phase catalytic processes.

Exploratory research on innovative catalytic concepts is a powerful tool for making major improvements. Exciting advances have been made in novel catalysts from metal alloys, alkoxide activation of CO and supported rhodium catalysts, and concepts of expert systems (artificial intelligence) for catalyst design.

9.3.3 **Process Economics**

9.3.3.1 General

Many detailed economic estimates have been made by experienced engineers for the manufacture of synfuels. The cost of production of synthetic fuels is much more dependent on plant investment costs than on raw materials costs. Considerable variations in estimates occur partly because costs of plant construction and of raw materials are quite site-specific. However, it is clear that, under usual industrial conditions, synfuel manufacturing costs are greater than costs for gasoline made from petroleum at present petroleum prices.

It is now rapidly being recognized that the value of a fuel can be strongly dependent on environmental criteria. These alter fuel economics. Higher environmental performance justifies higher prices. Thus, while the current price of gasoline at the refinery is 65 cents per gallon, MTBE (with an 87% rate of heat combustion) sells at 100 cents per gallon. It can be considered that fuel prices are determined by the following values: 1) heat of combustion, 2) octane or diesel rating, 3) environmental properties.

The main barrier to synfuels from syngas is their cost relative to gasoline made from petroleum at present day prices. As described in this report, there is the potential to lower the cost of liquid synfuels from syngas by new and improved catalytic synthesis technology which can:

- Lower the cost of manufacture by lowering plant investment costs
- Justify higher-than-gasoline price by providing improved engine performance
- Justify higher-than-gasoline price by providing environmental benefits (MTBE is an example) (Another example is zero sulfur, zero aromatics diesel fuel from syngas).
- Improve economics of synfuel manufacture by providing for high price coproducts: chemicals or electricity.
- Provide for liquid synfuels from biomass which are not subject to future tax on CO_2 emissions.

9.3.3.2 Economic Impact of Expected Improvements

It is reasonable to expect that the proposed research can provide technology which will improve economics of clean fuels manufacture by 10 to 30%. Realistic engineering studies have assessed possible improvements to be in this range. The use of a fixed fluid instead of a circulating fluid catalyst bed for manufacture of gasoline to decrease overall plant investment by 18% has been published by SASOL. This is illustrated in Table 1. Investment costs are the major contributors to synfuels manufacturing costs.

Use of a slurry catalyst reactor has been estimated to cut the cost of methanol manufacture by 10%. A further example of cost reduction is the estimate for combined use of a slurry catalyst reactor and an improved gasifier to manufacture gasoline and diesel fuel. The fuel cost improvement is about 30%.

Additionally, studies by Bechtel (Fox, 1993) confirm improvements of 30% possible in synthetic fuels manufacture by proposed new technology, *cf.* Table 2.

Table 1.
Capital Cost Comparison, Sasol Circulating, and Fixed-Fluid Bed Synthesis Units (Jager *et al.*, 1991)

Type	No. of Reactors	Pressure	Relative Capital Cost		
			Reactors	Gasloop	Total Plant
CFB BASE	3	normal	1.00	1.00	1.00
FFB	2	normal	0.46	0.78	0.87
FFB	2	high	0.49	0.71	0.82

Table 2.
Improvement in Indirect Coal Liquefaction (Gray *et al.*, 1992)

Configuration	Lurgi Gasifier + Synthol F-T	Shell Gasifier + Synthol F-T	Shell Gasifier + Slurry F-T
Efficiency %	44	55	59
Gasoline/Diesel Selling Price $ /Barrel	59	51	43

9.4 THE CATALYTIC PRODUCTION OF FUTURE FUELS

9.4.1 The Change From Conventional To Reformulated and Alternative Fuels

9.4.1.1 Driving Forces For Change

a. Reformulated Gasoline: Environmental concerns are requiring changes in the nature of the liquid transportation fuels that will be acceptable in the future. Vapor pressure restrictions limit butanes and other light alkanes to levels far lower than were acceptable in the past. Aromatics, in particular benzene, are undergoing restrictions as well. Both butanes and benzene are compatible with conventional fuel materials and provide high-octane and good drivability characteristics. Branched alkanes of five carbon atoms or more are deemed to be more environmentally friendly and can be used to enhance octane without violating vapor pressure restrictions or using aromatics. At the same time, oxygenates are mandated to meet standards of the Clean Air Act Amendment. Oxygenates, such as alcohols and ethers, have long been used as high-octane fuel components, so their introduction into future fuels will have the dual benefits of both a clean-burning and a high-octane product. Sulfur restrictions as well as removal of low level toxics will also be mandated. Thus, light hydrocarbons including butanes, benzene, sulfur, olefins, and low level toxics will be removed from the gasoline of the future. In their place will be greater levels of branched alkanes and alcohol or ether oxygenates.

(i) Oxygenates — Oxygenates will be a major source of clean-burning, high-octane liquid fuel materials in the future. Alcohols and the ethers that can be made from them are the oxygenates that are used to replace aromatics, reduce toxicity, and reduce ozone and carbon monoxide in the reformulated gasolines of the 1990s. As we will show, new catalytic chemistry for the direct air-oxidation of light alkanes to produce alcohol-rich oxidates could be developed to produce components of reformulated gasoline or liquid fuel alternatives to gasoline in areas where there is nonattainment of CO limits set forward by the Clean Air Act Amendment. In this way, light alkanes which are cheap, available from natural gas or refinery streams, and are rejected from the gasoline pool, might be converted into environmentally acceptable, high-octane quality fuels. Alcohols of the type that can be formed directly from natural gas or light refinery stream components are methanol, ethanol, isopropyl alcohol, and *tert*-butyl alcohol; they are not only useful as liquid fuel components themselves, but are used in the manufacture of ether oxygenates such as MTBE, TAME, and ETBE as well. Table 3 shows some of the fuel-related properties of the C_1 - C_4 alcohols and the ethers that can be made from them. It can be seen that these materials have desirable fuel properties in addition to meeting the fuel oxygen-content requirements of the Clean Air Act.

Table 3.
Properties of Ethers and Alcohols

Property	MTBE	TAME	ETBE	TAEE	DIPE	ETOH	GTBA	IBA	IPA	MeOH
Oxygen, Wt%	18.2	15.7	15.7	13.0	15.7	34	21.6	21.6	26.6	49.9
Sp. Gravity	0.74	0.77	0.74	0.764	0.73	0.79	0.791	0.81	0.789	0.796
Boiling Pt., °F	131	187	163	215	155	172	181	226	180	149
RVP (lbs/in^2)	7.8	1.5	2.5	1	4.9	2.3	1.8	0.6	1.8	4.6
Blending RVP	9	2	5	2	5	23	12	5	14	75
RON BV	100-112	111	117-121	106-112	—	122	103	-	113-119	126
MON BV	98-102	98	100-105	88-94	—	96	91	-	95-101	104
R+M/2BV	103-111	104	110	100	105	109	97	102	104-110	115
M Btu/Gal	93.5	100.6	96.9	—	100	76	94.1	95.1	87.4	56.8

MTBE = methyl tertiary-butyl ether
TAME = tertiary-amyl methyl ether
TAEE = tertiary-amyl ethyl ether
DIPE = diisopropyl ether
ETOH = ethanol
IPA = isopropyl alcohol
IBA = isobutyl alcohol

ETBE = ethyl tertiary-butyl ether
RVP = Reid Vapor Pressure
RON BV = research octane blending value
MON BV = motor octane blending value
GTBA = gasoline grade tertiary-butyl alcohol
MeOH = methanol
M Btu/Gal = thousands of Btu per gallon

As desirable as it is to convert light alkanes directly to alcohols, doing this in an efficient manner using existing technology is a major problem. The light alkanes, *e.g.*, methane, ethane, propane, and the butanes are among the most abundant and inexpensive raw materials. They are found not only in natural gas but also in light petroleum fractions and are being generated in ever greater quantities in petroleum refineries due to the increasing severity of catalytic cracking of heavier crudes. There exist few commercial processes for the efficient upgrading of these substrates to high-value products and no direct catalytic functionalization of these substrates with air or oxygen to produce chemical or fuel alcohols. New catalytic processes for accomplishing this are needed, and work in this area should be encouraged.

(ii) Branched Alkanes — Gasoline and its crude precursor contains substantial quantities of normal alkanes. These hydrocarbons have very poor octane blending values (R+M/2 <50). Addition of aromatics, oxygenates, and other high-octane additives offset the poor performance attributes of linear alkanes. Isomerization of n-alkanes increases octane by 30-40 numbers. A problem with current acid catalysts for isomerization is that activity is relatively low, and under isomerization conditions considerable cracking may occur. In addition, the milder the temperature, the more favorable is the branched/normal ratio. Thus, research which could provide a new generation of solid superacid catalysts for low temperature selective isomerization of normal to branched alkanes is of great interest.

As we have mentioned, large quantities of butanes are being removed from the gasoline pool. Isobutane is the main candidate for olefin alkylation reactions. Alkylation provides a generally highly branched hydrocarbon mixture having good fuel properties for blending into reformulated motor fuel. Current alkylation catalysts, H_2SO_4 and HF, are corrosive and environmentally hazardous. Again, an active solid acid catalyst for the efficient heterogeneous catalytic alkylation of olefins is needed. High acidity is also desired to make possible alkylation of the less reactive olefins like propylene.

We have discussed the need for olefins both as alkylation feedstocks and as fuel and chemical precursor materials. Dehydrogenation is an endothermic, high temperature catalytic technology, and improvements are needed. We will discuss the merits of oxidative dehydrogenation and suggest that catalytic research is needed in this area as well. In short, we must become more skillful at activating aliphatic C-H bonds, not only to oxidize or functionalize alkanes, but to rearrange or couple them, to give viable future fuel products.

b. Alternative Fuels — In addition to the reformulated motor fuels discussed above, more and more emphasis is being placed on whole fuel replacement/alternative motor fuels. Methanol is being used in fleets in areas of low attainment of air quality. Natural gas and propane have been used, as well as other unconventional fuel materials. Research support which fosters conversion of our plentiful coal reserves into fuel and chemical products is

> critical. Among the driving forces for alternative fuels is the desire for energy independence and the interest in utilizing cheap or available nonpetroleum raw materials. Research which enables us to broaden the available raw material base in an economic manner to make environmentally acceptable fuel materials will be of great benefit to the nation and to industry as well. New catalytic reaction chemistry has the greatest probability of helping to achieve this goal.

As we mentioned above, raw material availability is a major driver of alternative fuels. As petroleum reserves dwindle, all hydrocarbon raw materials which could be converted to liquid fuels become more dear. Often the search for oil yields extensive gas reservoirs. Gas availability on a worldwide scale rivals that of crude oil but problems of transportation and differences in end use application often limit its utility. Most natural gas is found in areas remote from its ultimate use. Currently, much of this remote gas is associated with petroleum production. Because it cannot be used at the location where it is produced, it is often flared on a large scale, representing not only a wasted energy resource but also contributing to global warming as a result of carbon dioxide production. Because of its low energy density, methane is relatively costly to transport. Figure 2 shows the relative differences between the costs of transporting various liquid and gaseous fuels (Parkyns, 1990). It is readily seen that the conversion of methane to a liquid fuel such as methanol or a hydrocarbon liquid would both drastically cut the cost of transport over long distances and provide an alternative fuel liquid from an abundant, under-utilized resource.

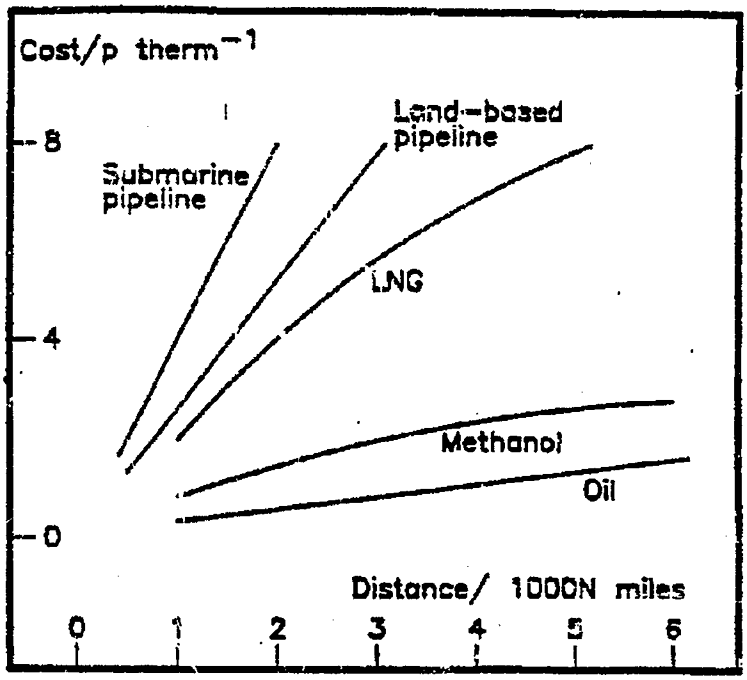

Figure 2. Transportation Costs of Liquid Fuels.

Catalytic alkane conversion science is maturing to the point that one can envision the economically attractive conversion of natural gas to liquid fuels on a commercial scale by the turn of the century. This situation has many international and national implications. Remote accumulations of low value gas such as exist on the North Slope of Alaska and various offshore sites could be exploited. Value could be maximized for domestic gas reserves in high value-added products. The national interests would be well served if the U.S. held the technological lead in gas conversion technology and could influence the course of gas conversion abroad. One of the most costly steps in the current technology for converting natural gas to liquid fuels is the energy-intensive steam reforming step. The products of steam reforming are catalytically converted to methanol which has value as an alternative liquid fuel product or which could be converted to gasoline *via* existing technology (Chang, 1977; Lee *et al.*, 1980; Walker, 1986). A new catalytic approach that permits the direct production of a methanol-rich oxidate from natural gas and completely avoids costly steam reforming is highly desirable. We will discuss research approaches aimed at such a goal in subsequent sections.

9.4.1.2 Roles of Catalysis in Providing Future Fuels

Table 4 indicates many of the ways in which energy-efficient catalytic processing can make major impacts on the way we produce fuel materials. Research must continue to produce more active catalysts, catalytic processes which are more selective, catalysts which provide new routes to fuel products from available alternative feedstocks, and finally process simplicity and efficiency. Inspection of Table 4 shows that catalysis is far from a mature field. Much must be learned if we are to use catalytic process technology to its full potential.

Consider, for example, the way we currently obtain both oxygenates and alkylate for fuel use. Unreactive alkanes are converted *via* energy-intensive endothermic processes to unsaturated intermediates; syngas or olefins (Table 4), prior to further reaction to produce alcohols or alkylate. If we were able to better catalyze the direct activation of the carbon-hydrogen bonds of alkanes, we might be able to directly convert them to alcohols or branched higher alkanes in a single exothermic energy-producing step. Such routes are considered in greater detail in other sections of this report.

Table 4.
Energy-Efficient Catalytic Processing for Fuels and Chemicals

High Catalytic Activity
- Permits less severe operating conditions (T&P)
- Greater throughput, smaller reactor size
- Lower capital and operating costs
- Milder conditions may allow higher selectivity
- Activation of available, low cost, unreactive feedstocks

High Reaction Selectivity
- Minimizes energy-intensive separations
- Reduces by-products and toxic emissions

- Less reactant required to provide a unit of product
- Eliminates high costs of environmental remediation

Alternative Feedstocks

- Feedstocks are often 60-70% of manufacturing costs
- Natural gas, coal, and biomass are among potential alternatives

Process Simplicity And Efficiency

- Fewer process steps
- Integration of steps
- Energy utilization, process heat, cogeneration

9.4.2 Catalytic Production Of Oxygenates For Alternative/Reformulated Fuels

We have considered the need for oxygenates in future fuels from several standpoints. Of those oxygenates that can meet future fuel requirements, alcohols and ethers stand out as the most important. Each fuel alcohol or ether, however, has its own set of properties which dictate both the nature and level of its usage as well as the kind of catalysis which is currently used or might ultimately be used to produce it. For this reason, we will discuss each major fuel oxygenate in the context of technology currently employed in its manufacture, the current catalytic research on new routes which is ongoing and should continue, and some long-range challenges for catalytic conversions which would require new science and technology.

9.4.2.1 Alcohols

a. Catalytic Production of Methanol

(i) Conventional Technology

Methanol is currently produced largely by the steam reforming of natural gas to synthesis gas, followed by the efficient catalytic conversion of syngas to methanol (Rostrup-Nielsen, 1975). Gasification of coal to produce syngas is another method also used but is at the present time less economically attractive (Khan *et al.*, 1993).

(ii) Improvements to Existing Technology

- Catalytic Conversion of Methane to Syngas — Catalysts are now being developed for the direct production of synthesis gas having a hydrogen to CO ratio of nearly the desirable 2/1 ratio for generating methane. These heterogeneous catalysts promote the reaction of methane with oxygen to give synthesis gas that would not require shifting (Schmidt, 1993). Work of this nature helps us to understand processes which already have commercial potential.

- Catalytic Conversion of Syngas to Methanol — Technology that will permit a higher conversion per pass of syngas will improve the economics of methanol manufacture. In current methods of manufacture, conversion per pass is limited by thermodynamics to 25% and in practice is about 10%. Expensive recycle is required. Several encouraging concepts for higher conversions per pass are being investigated.

- More Effective Heat Removal — If heat could be removed more effectively from the reactor, temperature increases that create hot spots, decrease methanol conversion levels, and shorten catalyst life could be prevented. A slurry catalyst system, LPMEOH, has been developed and operational parameters have been established in the laboratory and in a 10-ton-per-day pilot unit (Brown et al., 1991). Demonstrations on a larger scale are being proposed. Utilization of a fluid bed catalytic reactor for heat removal has been explored with some success.

- Methanol Removal from Reactor to Achieve Higher Conversion — Conversion of syngas to methanol is limited by thermodynamic considerations under present industrial conditions. However, the following schemes are proposed for removal of methanol from the reactor which would increase conversion and decrease or eliminate the need for expensive recycle (Mills, 1993):

  - Gas solid trickle flow reactor
  - Reactor system with interstage product removal
  - Condensing methanol principle

- Novel Catalysts for Methanol Synthesis -- These novel catalysts can be used at 150-180°C instead of the usual 250-300°C. They would permit higher conversion of syngas because of more favorable thermodynamic limitations at lower temperatures. Also, operation at lower pressure in less expensive equipment would be possible. Additionally, the possibility is offered that the expensive oxygen plant would not be required. Syngas made in an air-blown gasifier would be used and the nitrogen separated more easily from liquid methanol product rather than from gaseous oxygen. Unusually high activity catalysts have been discovered. These are based on metal alloys, $KOCH_3$ (methyl formate route), and supported platinum group metals (Pd, Rh). Although these catalysts have promise, each has practical problems. It is here that fundamental research can provide critical information and ideas.

(iii) New Catalytic Approaches

- Direct Conversion of Methane to Methanol — Considerable research is underway in an attempt to convert methane to methanol directly and bypass the costly steam reforming step. Although well integrated processes have been developed (Rostrup-Nielsen, 1987) for conventional technology through syngas, there is no escaping the fact that it is first necessary to conduct an energy intensive endothermic steam reforming step followed by a subsequent catalytic conversion step which has equilibrium limitations. It stands to reason that if one could directly convert natural gas in a single exothermic oxidation step in high yield, this would be more attractive than current routes. One would, in effect, supplant a two-step route having a costly endothermic first step with a direct one-step route which is highly exothermic and could cogenerate energy.

- Thermal Oxidation of Methane to Methanol — Over the past decade there has been a resurgence of work on the direct autoxidative conversion of methane to methanol. Research in the 1980s (Yarlagadda *et al*, 1988) suggested that rather high yields of methanol might be achieved from direct non-catalytic methane oxidation. Subsequent results have shown that yields are much lower than had at first been hoped for, and calculations from gas phase kinetic studies indicate that obtaining methanol in higher than 5% yield from gas phase radical processes is unlikely (Labinger, 1988). Laboratory studies fall far short of even this limited result. Catalysts have been developed (Durante, 1989) which initiate the formation of radicals which are largely expelled into the gas phase. Under some conditions, methanol yields approaching 5% methanol (70% selectivity at 7% conversion) have been observed but these are far short of commercial viability under most future scenarios. More work is needed to fully understand this important catalytic reaction area.

- Suprabiotic Catalyst Systems — Beyond Chemzymes — It is well known that methanol is produced from methane under mild conditions by enzymatic catalyst systems such as methane monooxygenase. The enzymatic systems have practical limitations because of the need for low temperature oxidation and for stoichiometric coreductants, among others. Synthetic biomimetic catalysts, dubbed chemzymes, can mimic enzymatic catalysis but suffer from the same two drawbacks. Recent studies indicate that it may be possible to mimic some of the characteristics of the biological systems while catalyzing alkane oxidations using only oxygen and no coreductant with catalysts which are robust enough to survive industrial process conditions. Although limited success has been achieved to date with methane, more easily oxidized hydrocarbons can be converted to their respective alcohols using this approach (Ellis and Lyons, 1990). What is now needed is further work both to enhance catalytic activity and to introduce hydrophobicity to expel product rapidly from the catalyst and increase alcohol selectivity.

- Electrophilic Metal Catalysts — Catalytic materials containing palladium, thallium or mercury centers in a molecular environment which enhances their electrophilicity have been shown to be capable of cleaving the C-H bond of methane. When this is done in the presence of a strongly oxidizing oxygen-atom donor such as sulfuric acid at elevated temperatures, methyl bisulfate is the resulting product. The formation of methyl bisulfate from methane occurs catalytically in the presence of palladium, thallium, or mercury containing catalysts (Periana, *et al.*, 1993). Hydrolysis of this intermediate produces methanol. In this way methanol has been produced from methane in 40% yield — a great improvement over the <5% yields generated in free radical gas phase processes. Further work is needed to develop systems which might be able to use molecular oxygen directly and which might work in less corrosive environments.

(iv) Coproduction of Methanol and Dimethyl Ether

- Higher syngas conversion per pass can be achieved by providing a catalytic system which produces a mixture of methanol and dimethyl ether, DME, in a single reactor (Brown *et al.*, 1991; Hansen and Joensen, 1991). This is a chemical method of removal of methanol from the reaction system. DME is synthesized by the sequential reaction:

$$2\ CO + 4\ H_2 = 2\ CH_3OH = CH_3OCH_3 + H_2O$$

Depending on the catalyst and conditions, CO_2 may be produced instead of H_2O. A combination of a methanol synthesis and a methanol dehydration catalyst is employed. DME has a number of applications for fuels and manufacture of fuels and chemicals. The development of mixed MeOH and DME manufacture is regarded as important new technology.

(v) Increased Energy Efficiency in Methanol Use

- If waste heat from an engine exhaust is used to provide the energy to convert methanol back to syngas, an endothermic reaction, the heating value of the syngas is larger than that of the methanol from which it is derived (Yoon *et al.*, 1985). A gain in energy efficiency of as much as 20% is possible.

b. Catalytic Production of Ethanol

(i) Conventional Technology

- Fermentation ethyl alcohol can be manufactured from sugar, starch, or cellulosic raw materials, utilizing yeasts. In the U.S., corn is currently the principal feedstock. The fermentation process yields a low alcohol content beer which is distilled to the azeotrope, 95% alcohol. Synthetic ethanol is produced by the direct process in which ethylene is hydrated over a phosphoric acid catalyst at about 400 C and 1000 psi. Overall yield of ethanol is greater than 97%. In the U.S., there is currently nearly 400MM gal/vr of synthetic ethanol capacity. Total ethanol capacity exceeds 1.4 billion gallons per year.

(ii) New Catalytic Approaches

- Homologation of Methanol — A significant amount of research has been carried out over the past twenty years on the reaction of methanol with synthesis gas to give ethanol and water. Homogeneous and heterogeneous catalysts have been used. An attractive aspect of this reaction is the cost of starting materials. Improvements in catalytic activity and reaction selectivity are still needed. Relatively little has been done on this reaction. Non-catalytic autoxidation of ethane gives ethanol in up to 50% selectivity (Gesser *et al.*, 1991) at low conversion (< 10%). No high yield catalytic conversion has been reported. This reaction, if it could be developed, would have a major raw-material advantage over the commercial synthetic route from ethylene. Both the suprabiotic approach and catalysis by electrophilic metal centers, reviewed above, may have potential here (Lyons and Ellis, 1991; Sen *et al.*, 1992) as well.

c. Propanol and Isopropyl Alcohol

(i) Conventional Technology

- Isopropyl alcohol is a chemical for which there is nearly two billion pounds of annual capacity in the U.S. It is not currently widely used as a fuel additive and its chemical usage is in decline. It has fine fuel alcohol properties, being a clean-burning, high octane additive with good water tolerance. Its current method of manufacture *via* hydration of propylene, however, provides a product which is rather costly for fuel use. Recent work (Mobil) has demonstrated that condensation of IPA with propylene gives diisopropyl ether, DIPE, which has good fuel oxygenate properties as well.

- Propanol, n-propyl alcohol is produced in much smaller volumes than isopropyl alcohol. All propanol manufacturing in the U.S. uses the oxo process in which ethylene is catalytically hydroformylated to propionaldehyde in the liquid phase using synthesis gas. The aldehyde is then stripped off and hydrogenated to the alcohol in a second process step. Because of the lower volume and greater complexity of the manufacturing process, propanol is much more costly than isopropyl alcohol. Thus, even though it has interesting fuel oxygenate properties, cheaper methods of manufacture would be needed for its usage in fuels to be significant.

(ii) New Catalytic Approaches

Olefin hydration and hydroformylation are mature technologies which have undergone decades of refinement and are practiced at a very high level of efficiency. Propylene, however, is rather costly and this results in a relatively high priced product. Thus, new approaches to the production of three-carbon alcohols could best benefit from a cheaper raw material. Direct oxidation of propane to either alcohol would provide an economical process for fuel production if the catalytic technology were efficient enough. However, no catalyst currently exists for accomplishing this reaction well at the present time.

- Suprabiotic catalysts have been shown to slowly convert propane to isopropyl alcohol, but yields are still too low to be practical (Ellis and Lyons, 1989). Novel electron deficient macrocyclic metal complexes of iron are active enough to homolyze the C-H bond, and developments in this field suggest that significant improvements are yet to come. Electron withdrawal from the macrocycle dramatically enhances the iron III/II reduction potential, increasing the activity of the complex for C-H bond homolysis. Incentive exists for implanting systems of this type into appropriate surface environments both for thermal and oxidative stability at high temperatures and to achieve the practical benefits of oxidations in the vapor phase. It is conceivable that suprabiotic systems could be developed that would prefer primary over secondary C-H bonds. Cytochrome P-450, an enzymatic *in vivo* catalyst, converts C-H bonds to C-OH moieties in the liver (Ortiz de Montilano, 1986). *In vitro* experiments on long-chain alkanes indicate a preference for terminal over internal C-H bonds and biomimetic catalysts in several surface environments possessing structural features which promote terminal attack (Herron and Tolman, 1987). Though quite long-range, work in this area may in time allow the direct functionalization of alkanes at the primary carbon atom in preference to secondary C-H bond activation leading to catalytic processes which could indeed produce propanol from propane.

- Electrophilic metal catalysts might also be expected to give preference to terminal over internal attack on a substrate such as propane. The stabilities of the intermediate metal alkyls, M-R, would be expected to increase as R goes from tertiary to secondary to primary. Thus, catalysts which operate by heterolytic cleavage of C-H bonds to generate M-R and a proton might favor terminal attack over internal attack and might give propanol from propane as the major product. Much work remains to be done in this area and the potential for catalysis is great. These systems seem well suited for heterogeneous catalysis although early versions are largely homogeneous. Because of the relative stability of primary and secondary metal alkyls, these systems are purported to be capable of higher selectivity in oxidative functionalization reactions since product is less susceptible to oxidation than is starting material (Labinger, 1988). Thus heterogeneous catalysts possessing tailored electrophilic transition metal sites have the potential for promoting interesting regioselective alkane oxidations with high selectivity.

d) Four-Carbon Alcohols (BA, TBA, SBA, IBA)

(i) Conventional Technology

A variety of catalytic processes produce four-carbon alcohols for use as fuel additives, additive precursors, and chemicals. Butanol is manufactured in over a billion pounds per year. The dominant technology is hydroformylation of propylene to produce butanol which is used exclusively for chemicals production. *Tert*-butyl alcohol, TBA, is a by-product of propylene oxide manufacture and is dehydrated to isobutylene which is converted to MTBE for use as an oxygenate in reformulated gasoline. TBA has been used as a high octane clean-burning fuel additive both in the U.S. and abroad. The other isomeric four-carbon alcohols, isobutyl alcohol, and *sec*-butyl alcohol are not made on a large scale. Isobutyl alcohol, IBA, has been proposed as a blending agent such as TBA and MTBE and can be dehydrated to isobutylene for MTBE manufacture as well (Mills, 1993).

(ii) New Catalytic Approaches

- Direct Catalytic Oxidation of Isobutane — A new series of suprabiotic catalysts, having iron in a perhalogenated macrocycle, have been shown to efficiently catalyze the conversion of isobutane to TBA with unprecedented rates and reaction selectivity (Ellis *et al.*, 1990; Lyons and Ellis, 1991). Since these catalysts homolyze C-H bonds, it is relatively straightforward to attack the tertiary C-H bond in preference to the primary C-H bonds in the parent alkane. If further developed, this new catalytic technology has the potential of decoupling TBA manufacture from propylene oxide production and producing a fuel oxygenate directly without a chemical coproduct. New catalytic technology of this type may be able to displace the costly dehydrogenation of isobutane to isobutylene for ultimate production of both alkylate and MTBE — prime components of reformulated gasoline to meet Clean Air Act standards. More research in this area is clearly warranted.

- Direct Catalytic Oxidation of Butane — Just as was discussed in the oxidation of propane, suprabiotic catalysts might be used to oxidize butane to either *sec*-butyl alcohol or butanol if they were sufficiently developed to have the regioselectivity of the biological systems. Heterogeneous catalysts having electrophilic metal centers might be made which could regiospecifically oxidize butane to butanol.

- Isobutyl Alcohol From Syngas — Isobutyl alcohol can be directly produced in catalytic reactions but the overall selectivity over known catalysts is not high (Mills, 1993). It has been found that recycle of methanol in mixed alcohol synthesis increases higher alcohol formation by homologation of lower alcohols. In syngas conversion the thermodynamically allowable isobutanol concentration is very high. Thus, it is becoming possible to modify catalysts and reaction conditions in such a way as to promote the direct production of IBA from syngas (Air Products). If successful, this approach could result in an alternative route both to fuel alcohols, isobutylene, and MTBE from syngas as a starting material.

e) Mixed Alcohols

(i) Conventional Technology

There was much enthusiasm during the 1980s for the production of mixed alcohols for use as octane enhancing components in gasoline blends. The following special catalysts were developed: 1) alkali modified copper methanol synthesis catalysts, 2) Co or Ni modified copper methanol synthesis catalysts, 3) MoS_x-based catalysts, and 4) supported platinum-group metals (Pd, Rh). A comprehensive technology base was developed and trial commercial production initiated in Italy. An extensive series of pilot unit tests were conducted in Japan using French/Japanese technology (Courty *et al.*, 1990). Processes are available for license. However at present, mixed alcohols are not regarded as promising commercially since they cost more to manufacture than methanol, and most importantly, the need for an octane-enhancing blending agent is being filled with MTBE, which is regarded as having better all-round properties.

(ii) New Catalytic Approaches

- Catalytic Oxidation of Mixed Alkanes — A number of alkane mixtures such as natural gas, LNG, NGL could conceivably be directly oxidized to a mixture of alcohols using catalysts such as those discussed above. Since these mixtures have light alkanes ranging from methane to the butanes and higher, it may be difficult for catalysts to operate selectively on a group of hydrocarbons having such a wide range of reactivity. On the other hand, co-oxidation of methane with ethane or propane seems to enhance methane autoxidation. Perhaps it is more realistic and practical to imagine operating on single gas components such as methane, ethane, propane, and the like. Direct conversion of natural gas to a liquid oxygenate in an efficient manner will require much new catalytic research and development.

9.4.2.2 Ethers

a) MTBE and ETBE

(i) Conventional Technology

- Methyl *tert*-butyl ether, MTBE, and ethyl *tert*-butyl ether, ETBE, are manufactured by reacting either methanol or ethanol with isobutylene. The isobutylene used for this reaction is either recovered from refinery processes or manufactured from isobutane by dehydrogenation or by oxidation processes, as described previously. We have already discussed new oxidation processes to produce isobutylene *via* TBA. Better and cheaper catalytic dehydrogenation systems for isobutylene production are also needed. Because of its use in providing fuel oxygenate to meet Clean Air Act standards for reformulated gasoline, MTBE is currently one of the largest and fastest growing chemicals in the U.S. and ETBE is beginning to be produced as well.

(ii) New Catalytic Approaches

- Direct reaction of TBA with methanol — Research is currently underway to develop a process for the direct production of MTBE *via* the acid catalyzed reaction of TBA with methanol in one step (Knifton, 1989). Current technology requires that TBA be first dehydrated to produce isobutylene which would then be reacted with methanol or ethanol to give MTBE or ETBE. Although it is not a difficult step, removal of the hydration reaction would provide process simplicity and reduce costs. Devising process conditions which will remove water of dehydration in order to shift the equilibrium toward ether will be of great benefit. Acid catalysts which operate efficiently in this process are being developed.

- Catalytic Dehydrogenation and Oxidative Dehydrogenation — Isobutylene is needed as a feedstock for conventional MTBE plants. It can be obtained from refinery processing or *via* dehydrogenation of isobutane. Catalytic or thermal dehydrogenation is the currently practiced technology for converting the lower alkanes to olefins. This technology, however, is faced with many challenges. Light alkanes are quite unreactive. Dehydrogenation is highly endothermic and large amounts of heat must be added to a reactor at very high temperatures. Equilibrium conversions are not high and very elevated temperatures are needed. This presents problems in achieving high reaction selectivity and affects catalyst life and activity as well as coking. Oxidative catalytic dehydrogenation does not have the thermodynamic limitation that catalytic dehydrogenation has, since the reaction is driven to completion by oxygen as a hydrogen acceptor. Oxidative dehydrogenation is exothermic and therefore the problem of adding large amounts of heat to the reactor at high temperatures is avoided. Heat released can reduce catalyst coking. Although alkyl aromatics can be efficiently oxidatively dehydrogenated, (ARCO, Phillips, UOP) and ethane will react with oxygen to give ethylene and water, much more catalyst development and process work must be done in the area of oxidative dehydrogenation before it can be applied broadly to light alkanes. Active selective oxidative dehydrogenation catalysts which can operate under industrially attractive conditions could provide breakthrough opportunities in isobutylene manufacture.

- Superior Isomerization Catalysts — Linear butenes from refinery processes and n-butane from natural gas are more abundant than isobutane. It has been found that butenes can be catalytically isomerized (Lyondell, 1992) to give isobutylene. Superacids have recently been developed which allow the rapid, selective low temperature isomerization of butane to isobutane which could be used as an MTBE feedstock, regardless of whether MTBE were made *via* dehydrogenation or oxidation routes. These superacids are based on activated iron substituted sulfonated zirconias and are the most acidic and active solid superacids known to date (Hsu *et al.*, 1992). More research and development on these fascinating solid superacids may be important not only for isomerization but for other catalytic applications as well.

b) TAME and TAEE

Tertiary methyl ether, TAME, and tertiary ethyl ether, TAEE, are high quality fuel oxygenates produced *via* acid catalyzed reaction of isoamylene with either methanol or ethanol, respectively. Isoamylene is a product of fluid catalytic cracking and is available in modest quantities in refinery streams. The driving force for converting isopentane to isoamylene either by dehydrogenation or oxidation to isoamyl alcohol followed by dehydration may not be as high as the analogous routes on isobutane. The reason is that isopentane is a high-octane, clean-burning branched alkane which has value as an integral part of the reformulated gasoline pool already. Nonetheless, catalysts which can selectively oxidize or dehydrogenate isopentane could give the olefinic precursor to TAME.

c) DIPE

Diisopropyl ether is a high-octane product having good properties as a fuel oxygenate. It is made by acid catalyzed condensation of propylene and IPA. A direct one-step acid catalyzed condensation of two moles of IPA would be a less costly alternative to this technology, if the IPA could be formed directly from propane by catalytic air oxidation, as previously discussed.

9.4.3 Alkylate And Branched Alkanes To Replace Benzene

a) Alkylation

(i) Conventional Technology

- Alkylation of olefins is conventionally carried out in refinery operations using either sulfuric acid or hydrofluoric acid as a catalyst. This catalytic reaction usually is used to alkylate mixed butenes with isobutane to produce a relatively high-octane hydrocarbon (<u>R+M/2</u> ≈ 90) to add to the gasoline pool. Branched alkanes are an effective way to add octane to reformulated transportation fuels in which aromatics, and in particular benzene, are backed out in order to meet environmental standards.

(ii) Current Research

- Solid Alkylation Catalysts — Solid alkylation catalysts have been under development in a number of laboratories for quite some time. Progress has been made with several novel systems, including MELS (King *et al.*, 1991), solid sulfonated zirconias (Hsu *et al.*, 1992; Hino and Arata, 1979), and others. A solid superacid which could smoothly alkylate an olefin with an alkane to produce a high octane nonaromatic transportation fuel material would be highly desirable from both an energy and an environmental standpoint. A superacid might increase the feed flexibility to allow alkylation of lower olefins and even allow the use of normal alkanes as alkylating feedstocks. A solid superacid which does not have the potential for HF release to the environment or the corrosivity of sulfuric acid systems would be an environmental boon. Advances in understanding and exploiting these new superacids are increasing and must be encouraged. More research on solid superacids in general and sulfonated zirconia, titania, and related oxidic systems should be undertaken for these reasons.

- Oxidative Dimerization of Light Alkanes [illegible] enormous amount of research has been conducted over the past decade on the oxidative dimerization of light alkanes with most of the effort focused on converting methane to ethylene (Keller *et al.*, 1982; Jones *et al.*, 1987; Driscoll *et al.*, 1987; Taylor *et al.*, 1988; Hutchins *et al.*, 1988). A variety of reducible metal oxides have been studied in both the presence and the absence of oxygen in a large number of reactor types. The driving force for this work was to convert natural gas to a liquid fuel material that could be easily transported and would be acceptable in the current transportation fuel system. Conversion of methane to ethylene, followed by subsequent production of liquid fuel from ethylene was a technology investigated by many groups. Much progress was made in understanding this reaction and yields of ethylene from methane exceeded 30%. Though not yet commercial and suffering from process limitations that may require a catalytic breakthrough, this work has come fairly close to developing practical technology. Work should proceed at some level in this area to continue to investigate applications to methane coupling but also coupling of other light hydrocarbons C_2 - C_4 into the gasoline range.

Other similar approaches were developed in which methane was oxychlorinated to methyl chloride (Mitchell *et al.*, 1992) followed by conversion of the alkyl halide to gasoline (IIT, PETC). Oxybromination chemistry has also been employed (SoCal) in the laboratory. Even higher yields could be obtained using this chemistry but problems associated with corrosion and halide contamination of products and the need for separations and new reactor technology are still among the things limiting this application. Again, the advances gained in being able to functionalize light alkanes in ways that were not possible at the inception of this work should encourage us to continue to pursue these and related catalytic reactions with the ultimate goal of being able to convert light alkanes either from natural gas or light refinery streams into higher value fuel and chemical products.

Another development which has occurred during the past decade is the ability to catalytically dehydrocyclize light alkanes, such as propane, to aromatic hydrocarbons. This kind of conversion is carried out over gallosilicate catalysts, most notably catalysts having framework substituted gallium in ZSM-5. Much research has been carried out (BP, Exxon) in an attempt to understand and apply this reaction chemistry. A small commercial unit capable of processing about 1000 bpsd of LPG has been built in Grangemouth, Scotland. As in the areas mentioned above, this work greatly extends our ability to manipulate aliphatic hydrocarbons; advances in the area will have impact on our energy future.

b) Isomerization of Linear to Branched Alkanes

Isomerization of C_4 - C_6 paraffins is an important technology practiced to convert streams with high normal paraffin content to branched alkanes and in so doing increase blending value octane numbers by as much as 20-30 points (UCC, BP, UOP, 1986). Isomerization is one of the least costly ways of producing octane barrels and is of importance as reformulated gasolines introduce octane *via* branched alkanes rather than benzene. A number of processes exist which use either platinum on amorphous supports or use zeolitic versions (UOP, IFP). The technology is in place around the world and is at a relatively high level of development. Superior catalysts which will allow low temperature operation, where equilibrium favors the branched relative to the normal alkanes, will be of value. In a subsequent section we have reviewed the recently patented superacid catalysts (Hsu, 1992) which are the most highly acidic known to date and are capable of rapid low temperature isomerization of butane. Furthermore, these catalysts are able to isomerize higher alkanes with little cracking. Continued improvements in solid superacid chemistry are of importance in replacing corrosive and toxic analogs from the environment. Many refinery operations currently use acid catalysis, and much of this technology is mature. Some of these processes would benefit from superacidity. Major advances in solid superacid chemistry could have an extremely beneficial effect on refinery processes of the future.

9.4.4 Hydrocarbon Fuels from Syngas

9.4.4.1 Fixed Fluid Bed Fischer-Tropsch Synthesis Reactor

The Fischer-Tropsch process has long been employed for production of gasoline from syngas, notably in Germany in WW II and in South Africa (SASOL), beginning in 1954. Recently, important new and improved technology has emerged, unexpectedly perhaps, since FT is such a long and well researched process.

SASOL announced in 1989 that a fixed fluid bed catalytic synthesis reactor had been installed (Dry, 1990). It is reported that this cuts the cost of the synthesis plant section in half, relative to the previous entrained fluid bed reactors. Improved plant operability is also reported. SASOL has also indicated that a slurry phase reactor system will be operated in 1993.

9.4.4.2 Synthesis To Wax, Hydrocrack To Diesel And Gasoline

Royal Dutch/Shell, Amsterdam, is constructing a 14,000 bpd plant in Malaysia at a cost of $660 million. A novel combination of catalytic processes is employed in the Shell Middle Distillate Synthesis (SMDS) process (Sie *et al.*, 1991). Syngas from natural gas is converted to high molecular weight waxy hydrocarbons. It appears certain that a cobalt catalyst will be used, operated under conditions that provide for conversion to high molecular weight hydrocarbons (high alpha value; Anderson-Shulz-Flory constant) in the synthesis process. A key feature is the avoidance of production of low molecular weight hydrocarbons, particularly methane. The waxy product is selectively hydrocracked, using modern hydrocracking catalysts, to produce high quality diesel fuel, valuable waxes, and gasoline.

The Exxon Corporation has been active in developing a new process for synthesis of hydrocarbon fuels from syngas. Almost nothing has appeared in technical literature. However, Exxon has said to stockholders that its divisions are "collaborating on advanced proprietary technology for on-site conversion of natural gas to liquid products". They have named it AGC-21 — Advanced Gas Conversion for the 21st Century (Eisenberg *et al.*, 1993). A demonstration unit is now in operation "obtaining critical data for scale-up to commercial size". An investment of over $100 million has been made over a ten-year period and more than 100 patents have been obtained. It appears that this is also a variation in the FT-type process. It is reported that a new fluid bed gas reforming process has been developed. Exxon has said that the syngas is converted to an intermediate product. This may consist of C_{5+} hydrocarbons which are isomerized and/or hydrocracked to produce a gasoline having suitable octane rating, and other products, such as diesel fuel (Eisenberg *et al.*, 1993).

9.4.4.3 Slurry Phase Fischer-Tropsch (FT)

One of the most exciting developments in FT technology is the slurry phase conversion of syngas to hydrocarbon fuels. Originally investigated in Germany by Koelbel following WW II, recent engineering and economic evaluations have given great impetus to the possible advantages of slurry phase FT. A major improvement is the capability to carry conversion-per-pass nearly to completion and so avoid major recycle costs. It has been recognized that information obtained on a larger-scale unit is needed. An important test was carried out in August 1992 in the La Porte, TX, unit, sponsored by DOE and a number of national and international industrial partners. Slurry phase FT operation is being conducted on a very small scale in a plant operated by the Fuel Resources Development Company near Denver. An iron-based catalyst is used and the diesel fuel product has been reported to have excellent properties.

9.4.4.4 Methanol-to-Gasoline and Related Processes

The Mobil MTG process (methanol-to-gasoline), developed cooperatively with DOE, has been in successful operation in New Zealand for six years. Improvements in the MTG process have been made since its installation in fixed bed form. The H. Topsøe Company has developed the Topsøe Integrated Gasoline Synthesis (TIGAS) process by operating all these steps of the MTG process — syngas production, methanol synthesis, and conversion — at the same pressure and the last two steps in a single synthesis loop (Rostrup-Nielsen, 1987). Also, with support from DOE, a fluid bed version of MTG has been demonstrated on a semi-commercial scale in Weseling, Germany. Furthermore, the related MTO (methanol-to-olefins) and MOGD (Mobil olefins to gasoline and distillates) processes have been developed.

9.4.5 Synthetic Fuels from Coal, Petroleum Residuals, Heavy Tars, and Biomass

Even though the analysis contained in this section concludes that the hydrocarbon feedstocks discussed have lower priority in the current 10 to 20 year projects, research that promises significant advances in the application of heterogeneous catalysis to their conversion to liquid transportation fuels should continue. That research should focus on fundamental aspects and those of catalytic process engineering which could substantially alter the economic or environmental debits associated with these feedstocks. We divide this group into two categories. The first group contains coal, residual oil, and heavy tar sources. This group, while representing a considerable strategically secure resource, suffers from high environmental and economic constraints on production, transportation, and conversion to liquid transportation fuels. At this time, shale oil is excluded because the environmental and economic constraints seem even more severe. The second group contains biomass as the source for liquid transportation fuels which has the potential advantage of being CO_2 neutral.

9.4.5.1 Synthetic Fuels from Coal, Residual Fuel Oil, and Heavy Tars

Of this group, residual oils are currently available for conversion as a by-product of petroleum refining and could be converted without further production costs, providing that appropriate catalytic removal of sulfur and other pollutants occurs. Currently, these oils are burned for fuel and are limited in quantity because lighter crudes with small residual components are used in the refinery. Should a process be developed for conversion to liquid fuels, larger quantities could be obtained by using heavier crudes in the refinery. Processes exist for conversion of these feedstocks to liquid fuels, but they require large amounts of hydrogen for conversion. This is characteristic of this group. More efficient use of hydrogen and cheaper sources of hydrogen are required. Currently, hydrogen is obtained in the refinery as a by-product of reforming reactions. Large-scale conversion of feedstocks in this group will require additional sources of hydrogen. Research to discover alternate catalytic routes to hydrogen should be a high priority.

Hydrogen distribution among the molecular fragments produced thermally remains a fundamental issue in converting these feedstocks. It is known that small amounts of added catalysts can greatly increase the amount of liquid products which result from a hydroconversion process. This effect is poorly understood, and recycle of the catalyst particles is still an issue in order for these processes to be economical. Research should be supported at a fundamental level to understand the role of small amounts of catalyst in hydroconversion processes.

Coal and heavy tars differ from residual oil conversion only in the fact that they contain smaller amounts of inherent hydrogen, with coal being the most hydrogen-poor feedstock. All these feedstocks contain large amounts of sulfur and nitrogen which makes the resulting liquids difficult to hydroprocess. They also contain large amounts of aromatic compounds. Coal in particular yields a highly aromatic product, requiring intensive further hydrogenation of the resulting liquids. Research in this area should focus on novel catalysts which remove sulfur and nitrogen during liquefaction. This requires catalysts that are robust, inexpensive, and recyclable.

Residual oil and heavy tars often contain organically bound metals which make catalytic processing extremely difficult. The metals include typically V and Ni which, in addition to clogging catalysts, represent a disposal problem after conversion. Catalytic conversion of these feedstocks will require novel approaches to handling these metals as well.

Production of Liquid Fuels from Coal

Direct liquefaction of coal is proven technology which can be used if the price of petroleum exceeds 30$/bbl and if environmental limitations can be addressed. The current best technology can yield more than 50% distillable liquids from coal on a m.a.f. basis, or 70% if the required hydrogen is made from methane, with the process operating at better than 2000 lbs. of H_2 pressure. The liquids obtained from direct liquefaction require further upgrading for removal of sulfur and nitrogen. Coal liquids are also highly aromatic and will require extensive hydrogenation to meet environmental regulations. These two tasks require the same catalysts as described above for sulfur removal and aromatics saturation.

Increasing the liquid yield at lower hydrogen pressure will further improve the process. This will require better catalysts. Direct liquefaction catalysts are needed to more effectively shuttle hydrogen to thermally produced free radicals which otherwise may polymerize to produce non-liquid or heavy products.

The catalyst may be added to the liquefaction reactor in small quantities to modify the hydrogen pathway. Transition metals have been used for this purpose but are quickly converted to sulfides, which are the active catalysts.

A major cost of liquefying coal is the hydrogen required. Measures which utilize the hydrogen more efficiently, such as described in the previous paragraph, are advantageous. Catalytic ways of producing cheaper hydrogen would be of great benefit. Processes which combine methane and coal would also enhance the liquefaction of coal. This would require a catalyst which activates methane in the presence of coal. In summary, improved direct liquefaction processes require the following catalyst improvements:

- Improved hydrodesulfurization, hydrodenitrogenation, and aromatics saturation catalysts
- Improved hydrogen transfer and radical healing catalysts
- New catalytic processes for producing hydrogen and utilizing inexpensive sources of hydrogen in direct liquefaction. The BP-UOP Cyclar process may be a good place to start the search for an improved process.

9.4.5.2 Synthetic Fuels from Biomass

The concept of manufacturing liquid fuels from biomass is appealing because it would shift part of U.S. energy consumption from petroleum to feedstocks that are either renewable resources or the inevitable waste products of modern society. Currently, ethanol derived from corn or sugar cane is used to a limited extent in transportation fuels in the U.S. and Brazil.

An attractive scenario for fuel production from biomass can be based on organic wastes such as corn cobs, bagasse, wood chips, garbage, and sewage sludge. These materials ordinarily require disposal at some cost to a business or community. If these wastes can be transformed from liabilities to assets as feedstocks for fuels, the economics and societal impacts can be highly positive.

The most generally applicable approaches to converting biomass to fuels involve multiple steps, some of which are not catalytic. Some liquefaction processes have converted some of the heterogeneous solid wastes to gases that can be purified before conversion to useful fuels, such as gasoline or diesel oil. Fortunately, there is a solid base of experience in conversion of organic wastes to methane-rich gases at several municipal waste facilities in the U.S. These gases, which contain methane, carbon dioxide, and inerts, can be feedstocks for several fuel production processes, described elsewhere in this chapter. The most immediate application is reforming landfill gas to synthesis gas that can be converted to fuels by the technologies described above. In fact, a small plant near Denver has begun production of diesel fuel from landfill-derived synthesis gas, using a slurry catalyst (Mills, 1993). In the long term, direct oxidation of the methane to methanol or oxidative coupling to form higher hydrocarbons may be more economical approaches. In either approach, the catalytic technologies are simply those being developed for natural gas conversion. The catalyst research outlined above is directly applicable to the utilization of biomass-derived methane.

A second major approach to using biomass as a fuel feedstock involves direct reforming to give synthesis gas which, in turn, can be converted to liquid fuels by the catalytic processes discussed above. The direct transformation of solid organic waste to synthesis gas is likely to involve reforming technologies like those used in the gasification of lignite, a technology that has received extensive study. The purified synthesis gas can be converted to methanol, mixed alcohols, or hydrocarbons by the catalytic processes described above. The research needs for this kind of catalyst development have been previously explained.

The production of synthetic fuels from biomass by either of the approaches mentioned above is likely to be less economical than production from natural gas or coal, because biofeedstocks have inherently lower energy contents. In addition, because the concentration of the biofeedstock in any one location is low (apart from municipal wastes in major metropolitan areas such as New York City), transportation costs for the feedstocks may be significant. The inherent economic disadvantages, however, are offset to some extent by reducing the disposal costs for biological materials that are regarded as wastes. The high costs for incineration or landfilling of municipal wastes may be adequate incentive to use them as feedstocks for fuels. For any specific biowaste, it is necessary to evaluate the costs of direct energy extraction by incineration with heat recovery *vs.* the value of the organic waste as a feedstock for fuel production. Similarly, methane-rich gases collected from a landfill can be used as a fuel directly, rather than being converted to a liquid fuel for sale.

Overall, the catalytic research needs for the most promising options to produce liquid transportation fuels from biomass are those required to produce synthetic fuels from natural gas or coal. Other options based on crops such as canola (rapeseed) are specific to the individual crop. Production of such fuels generally incur most for their costs (both in dollars and energy input) in the growth, harvesting and physical processing of the biomass. The catalytic treatment of the resulting oils is usually simple hydrogenation, a technology well developed for the production of cooking oils.

9.5 FUNDAMENTAL ISSUES IN LIQUID FUELS HETEROGENEOUS CATALYSIS

Research areas addressing questions of interest to specific classes of catalytic materials were outlined above. In this section, we list some fundamental questions which are general research questions underlying the phenomenon of catalysis by solids. Progress in answering these questions can lead to a new fundamental underpinning for the field of heterogeneous catalysis. Evidence suggests that, with the current generation of catalytic materials, we have only accessed part of the activity and selectivity inherent in catalysis by solids. Further improvement in the basic understanding of catalysis by solids can lead to a new generation of catalytic materials and catalysts with greater activity, selectivity, and stability. In order to achieve this however, a deeper probing of the catalytic phenomenon must occur and some deeply held ideas regarding catalytic behavior must be challenged.

9.5.1 The Role of Crystalline Active Catalytic Phases

It has been shown that on a per site basis the activity of unsupported MoS_2 is greater than that of supported MoS_2 and that the per site activity of well crystallized MoS_2 is greater still. Crystalline zeolitic materials exhibit stronger acidity than amorphous solids of similar composition. Yet commercial catalysts are often found in disordered states due to the desire to produce small particles of high surface area. Supports are usually included to increase the dispersion of metal and sulfide catalysts and to lower their cost. But evidence suggests that in most cases the support reduces the intrinsic activity of the active phase. This leads to several basic areas of research:

- The effect of crystalline order versus disorder in active catalytic phases.
- The effect of support interactions on the per site activity of the active phases.
- Methods of stabilizing small crystalline particles of active materials and forming them into useful catalytic particles.

9.5.2 The Role of Delocalized Electrons in Small Catalytic Crystallites

The active site has been the "Holy Grail" of catalytic science. Yet it is known that it is incorrect to view the catalytic solid as an array of single organometallic clusters. Catalytic solids often exhibit different and sometimes superior properties than related organometallic compounds with a small number of metals. In addition, organometallic compounds cannot usually be stabilized under conditions necessary for the catalytic processes described in this chapter.

Recent developments in the field of nanophase materials demonstrate clearly that crystallites in nanoscale range (1-10nm) have different and more useful properties than macrocrystalline or amorphous versions of the same material. Closer examination reveals that many familiar catalyst systems such as ammonia synthesis and sulfide catalysts are nanophase materials in their most active form.

The above suggests that delocalized electrons play an important role in the catalytic activity of metallic and semiconducting active phases. Several research areas of general interest arise from this point of view:

- Investigation of active nanophase material in catalytic environments.
- The role of immiscible solid catalytic phases in forming interfaces of catalytic interest. Examples are promoted sulfide interfaces, noble metal bimetallic cluster interfaces, *etc*.
- Surface phases formed under catalytic conditions. An example is carbide surface phases on metals.
- The role of delocalized electrons at catalytic surfaces.
- The role of bulk electronic structure in determining surface electronic properties.

9.6 OTHER ENVIRONMENTAL ISSUES IN LIQUID TRANSPORTATION FUELS HETEROGENEOUS CATALYSIS

Several other issues arise which are related to the use of producing liquid transportation fuels efficiently and safely. The solution to these issues presents important obstacles which may determine which catalytic approaches will be successful and which will be hindered. The researcher should be aware of them and research should be undertaken to assist in their resolution.

9.6.1 Environmental Uncertainties Regarding Alternate Fuels

A complete picture of the potential use of alternative fuels requires consideration of the long-term environmental effects of introducing large amounts of new fuels into the environment. It probably could not have been anticipated that chlorinated hydrocarbons would so adversely affect the environment. In the same way, we do not know the full effect of introducing a new fuel, such as methanol, into the environment. Research will eventually answer the question as we get to know the alternate fuels as well as we know hydrocarbon fuels.

In the same manner, the entire environmental cost of producing a new fuel must be considered. In switching to a new fuel, do we lower fuel efficiency to such a point that the environmental benefits are lost? When considering the overall process efficiency, do we consider the net environmental benefit? For example, does the environmental cost of farming outweigh the benefits gained from producing a "renewable resource" such as ethanol. Indepth studies of these questions should be carried out.

9.6.2 Biodegradability of Alternate Fuels

Fuels are inevitably spilled or lost. It must be established that the fuels are safely biodegradable as they enter the environment. Some ethers are reported to be strongly resistant to biodegradation. The biodegradability of oxygenates, such as MTBE, must be firmly established. This will allow confidence in the product and provide simple cleanup methods like bioremediation to be used on eventual spills. Auxiliary research should be performed to establish the biodegradability of alternate fuels.

9.6.3 Catalyst Disposal

The problem of disposing of or recycling used catalysts is becoming critical. The refiner can no longer bury these catalysts in landfills or on refinery sites. New methods are needed to recover metals from spent catalysts. Research in chemical or biological methods should be encouraged in order to be able to do this.

9.7 CONCLUSIONS AND RECOMMENDATIONS

Recommendations are summarized in this section. They are divided into short-term, middle-term (5 to 15 years), and long-term (beyond 15 years). Short term recommendations are already being implemented in many cases by industry and proposed research should impact on the middle- and longer-term recommendations.

9.7.1 Short-Term Recommendations

- Improved catalysts and improvements to existing processes to reduct aromatics, sulfur, nitrogen, and other pollutants.
- Improvements to catalytic processes to reduce pollution in the refinery.
- Improved catalysts and catalytic processes to provide oxygenates such as MTBE.

9.7.2 Middle-Term Recommendations

In this period the trend will continue to demand cleaner liquid transportation fuels based on petroleum hydrocarbons. Oxygenated hydrocarbons will continue to become a larger fraction of the total liquid transportation fuel supply. Methane and natural gas will become alternate sources of the liquid transportation fuel supply. Environmental demands on the refining processes themselves will become greater. This will require:

Highest Priority — Necessary for Success

- New catalysts and processes for the cleaning and conversion of CH_4 and natural gases to fuels and chemicals.

Medium Priority — Will Enhance Success

- New catalysts and new processes to provide very clean hydrocarbon based liquid transportation fuels which contain the minimum aromatics, sulfur, nitrogen, and other pollutants.
- New catalysts and processes which provide increased levels of oxygenated fuel supplies.
- New catalytic processes which are highly efficient and have low emissions at the refinery.

9.7.3 Longer-Term Recommendations

In this period, alternate fuels will begin to make a major impact on the hydrocarbon liquid transportation fuel supply. High-cost petroleum supplies will make alternate fuels based on secure resources such as coal, shale, and residual oil, more attractive. Introduction of a global carbon tax may make biomass attractive as a CO_2 neutral alternate source for making liquid transportation fuels. This will require:

High Priority — Necessary for Success

- New catalysts and catalytic processes for utilization of CO_2.
- New catalysts and catalytic processes for the production of H_2.

This includes better utilization of hydrogen, non-fossil sources of hydrogen, and new catalytic routes to hydrogen which do not yield CO_2 as a product.

Medium Priority — Will Enhance Success

- New catalysts and processes for producing methanol, ethanol, and other oxygenated alternate fuels

Lower Priority — Not Likely to Impact within Horizon of this Study

- New processes for cleanly converting coal, shale oil, and residual oil.
- New catalysts and catalytic processes for converting existing biomass feedstocks (carbohydrates) to liquid transportation fuels.

9.7.4 Recommendations for Catalyst Research

In this section are listed some recommendations covering specific areas of catalytic materials research.

9.7.4.1 Zeolites

For zeolitic catalytic materials the following areas of research are considered to be of major importance:

- Structure/catalytic function relations for existing zeolites and environmentally important fuels reactions.
- A continually increasing understanding of acidity in zeolitic catalysts.
- A better understanding of zeolite structure and phase relationships as provided by advanced probes and theory.
- A better understanding and control of zeolite synthesis and catalyst preparation.
- The discovery of new zeolitic materials and their relation to catalytic reactions of interest.
- Development of zeolitic materials for reactions specific to environmental fuels issues.

9.7.4.2 Sulfides

For the transition metal sulfides to continue to improve in activity and selectivity the following research areas are required:

- A continued effort to apply theoretical techniques to understanding the fundamental origins of catalytic phenomena in the transition metal sulfide catalytic materials.
- A continued development of an understanding of the promoted system with an ability to optimize activity or extrapolation to new catalytic systems.
- A continued development of structure/function relations in this system with an emphasis on larger molecules which represent the most important barriers to new levels of sulfur removal.
- Development of an understanding and optimization of the sulfide ability to catalyze aromatic hydrogenation in the presence of sulfur.
- Development of characterization techniques which can reliably characterize disordered sulfides.
- Development of new catalytic processes which take advantage of the sulfide's ability to both desulfurize and saturate aromatics simultaneously.

9.7.4.3 Metal Catalysts

Research is recommended in the following areas of metal catalysts:

- Understanding of the basic structural chemistry of small noble metal clusters needs to be developed. Bimetallic clusters and the interfaces of noble metal particles in their catalytic state need to be advanced.
- Theoretical and structural probes which relate to the nobel metal catalysts in their real highly dispersed states need to be advanced.
- Structure/function relations need to be developed which are related to small particles of noble metal catalysts for reactions of environmental importance.
- New noble metal catalysts need to be developed based on the fundamental principles outlined above. This may include an understanding of the role of 4 and 5d electrons and how noble metals may be replaced by cheaper metals.
- The role of carbonaceous overlayers needs to be elucidated and the learnings applied to develop new catalysts.

9.7.4.4 New Catalytic Materials

Research in new catalytic materials, such as oxides, carbides, and solid acids, should be pursued (see chapter 2). Research on these catalytic materials should focus on materials which are stable under catalytic conditions, occurring during production or refining of hydrocarbon based liquid transportation fuels. Research should also occur in areas related to the production of new catalytic materials such that useful materials can be made in large quantities at reasonable cost.

New Catalytic Materials for Novel Processes

Catalysts should be developed which operate in nonconventional reactor systems. These include:

- Slurry catalysts which operate effectively as small particles or crystallites in reactors producing oxygenates from syngas.
- Fluid bed catalysts which operate effectively in reactors producing oxygenates from syngas and removing heat effectively during reaction.
- Nanoscale catalysts for direct liquefaction of coal.

New Catalytic Materials for Oxygenates

In addition to the classes of materials outlined above, new catalytic materials and catalysts are needed for the production of oxygenates. Methanol catalysts are needed which reduce reaction temperature for more favorable thermodynamics.

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