Appendix A

REVIEWERS: COMMENTS AND ISSUES

A wide spectrum of experts reviewed the second draft of this report. The executive summary and appropriate chapters have been revised to incorporate most of the suggestions from these peer reviewers. The knowledge and insight provided by the reviewers has contributed greatly to the quality and completeness of this final report.

Generally, the reviewers found the report to be authoritative and the panel well qualified to provide research recommendations on subject. There was agreement with most of the report but some expressed opinions that certain items could have been emphasized to a greater degree. Generally, concerns about recommendations were said to be more a matter of degree than a matter of disagreement.

Some of the comments could not readily be adequately incorporated into the report and, as mentioned, some difference in opinions have been expressed in proposed research emphasis. These issues and comments are summarized in this appendix.

Hydrogen

Several reviewers agreed with importance assigned to research for hydrogen manufacture but thought that more definite research should be proposed, particularly for processes which do not involve CO_2 production. The following comments concerning hydrogen were made:

I was surprised and disappointed to see very little emphasis on the production of H_2. It is clear that there are insufficient supplies of hydrogen in our refineries. What is needed is a simple way of producing hydrogen from water. I thought the report could have been more ambitious (such as primary alcohol synthesis, production of hydrogen, stronger academic/industry interfaces).

The discussion of hydrogen does not indicate the source of hydrogen. Pure hydrogen is CO_2 - neutral only if produced from solar or nuclear energy. The report should indicate what route is proposed.

A theme that appears in several places in the report is that ways are needed to make hydrogen more cheaply. However, other than industrial advances in steam reforming of natural gas, the pace of advances in this area is very slow and clues are not furnished as to how this is to be accomplished.

Environmental

The following comments regarding environmental aspects were made:

You adopt the premise that the petroleum area will be driven by environmental concerns, yet almost no recommendations for work on catalytic control of emissions and many pages of recommendations for R&D in fuels strikes me as a contradiction. The report recommends leaving to industry work on catalysts for emissions control and goes deep into industrial processing of fuels.

A recognition also needs to be made that there is still a controversy on the effectiveness of oxygenates to control auto emissions without contributing to the problem. Mention should be made of the development of a superior catalytic auto exhaust muffler capable of operating at high efficiency under cold start conditions with complete conversions of pollutants to carbon dioxide and water. Such devices are currently under development and a successful system would have drastic effect on the economics of reformulated gasoline. This would be a killer technology for much of the anticipated catalysis and process innovations needed to meet future auto emissions standards.

Another repeated theme is — do something to cut down on CO_2 emissions or find uses for CO_2. Yet many of the reactions advocated (water-gas shift, Fischer-Tropsch, etc.) form CO_2. As practiced with iron catalysts, the Fischer-Tropsch reaction releases one CO_2 molecule for each $-CH_2-$ formed.

Direct/Indirect Coal Liquefaction.

The following comments concerning direct/indirect coal liquefaction were made:

One general concern is the report's emphasis on synthesis gas chemistry for the production of liquid fuels, with corresponding de-emphasis for direct coal liquefaction and heavy oil upgrading. We are less convinced than the authors about a trend toward or reliance on methane for liquid fuels. Gas prices have tended to follow petroleum prices, while coal prices have been flat. Moreover, coal supply is assured, while an inexpensive gas supply is less certain. Therefore, it is believed that greater opportunities exist than this report would suggest for improvement in direct liquids production from coal and heavy oils through catalysis research.

Surface Science

The following comments regarding surface science were made:
Personally, I believe that there is an over-emphasis on surface science and characterization of materials. Findings put too much emphasis on the rational design of catalysts. I believe computer modelling is being oversold nationwide!

The list of needs in science of catalysis is really surface science focused. We also need to establish new chemistry which will be possible with catalysis. There is too much analysis of catalyst surfaces and not enough evaluation of their utility. Many publications discuss the characterization of a catalyst without offering comparative data for the use of that catalyst compared to current catalyst alternatives. We need to put more chemistry back into catalysis.

It is a big leap from the arduous empirical concoction of a fluid cracking catalyst to the design and synthesis of a complex catalytic material. It would be good to make an honest statement about this complexity and the magnitude of the challenge ahead, and to develop with concrete evidence the reality of catalyst synthesis as it now stands, even if it is only primitive, and from this to develop what catalysis synthesis can be. It is important to develop the case with evidence, rather than asserting it.

The chapter on chemicals focuses on selective oxidation and that is appropriate. What is absent is a more ambitious quest for new chemistry. For example we need to discover catalysts for adding O_2 or water to olefins to produce primary alcohols. We need better catalysts for higher yields of sulfuric acid from SO_2. We need catalysts to produce phenol from benzene and O_2, to produce H_2O_2 from H_2 and O_2 directly, and propylene oxide via O_2 and propylene.

Economics

The following comments concerning economics were made:

We believe that the main barrier to commercialization of technologies which process these feedstocks is processing costs, not environmental concerns. Catalyst development could have a significant effect on reducing processing costs. It is clear throughout this report that the authors recognize that improvements and trade-offs must be considered in economic terms, but the treatment of economics is qualitative and inconsistently applied. While we recognize the difficulties in doing a comprehensive analysis of such a broad topic, we recommend that more formal attention be paid to defining and addressing economic issues in setting research priorities.

The point is made that advanced U.S. technology is important to improve the national balance of trade. Assume that many millions of dollars are funded to tackle the objectives outlined in this report. Will the researchers publish, patent, or give industry the rights to obtain patents? The current system suggests that the results will likely be presented to the science community for all nations to develop and commercialize with no real opportunity for U.S.-based industry. There should be a recommendation on how the panel would like to see intellectual property, funded through this research, provided to U.S.-based companies who pay some to the taxes which fund this research.

There is a sense of by-passing reality in the report. Research in catalysis is governed by industrial needs and by political decisions. Certainly the report recognizes the constraints imposed by the Clean Air Act Amendments and other legalities. But it does seem, for instance, to advocate that ethanol be synthesized from ethylene with barely a hint that there is a federal tax benefit of fifty four cents per gallon of ethanol made by fermentation of starch and later, from cellulose.

Other Specific Topic Comments

The following comments were made on other topics:

The anchoring of homogeneous catalysts to make heterogeneous catalysts was briefly alluded to. Perhaps more emphasis should be placed on this concept. This may be the fastest approach to developing new heterogeneous catalysts for difficult reactions. New approaches need to be discovered to truly anchor organometallic compounds without losing their homogeneous activity and selectivity.

Throughout the different chapters, I found a concern for the sulfur problem, but it is not given sufficient weight in the summaries. We need to uncover new chemistry to treat this sulfur and/or convert it into acceptable byproducts.

Ab initio calculations are an area of potential increased collaboration between national laboratories, with massive computing power, and industrial and academic researchers. Mention should be made of more close collaboration between academia/industry/government as a potential for making more rapid progress in several areas of catalysis.

Appendix B

PROJECT OBJECTIVES AND METHODOLOGY

BACKGROUND

In response to a Notice Inviting Grant Applications (Notice 92-7 published in the Federal Register, Vol. 57, No. 13, Tuesday, January 21, 1992, Page 2272), Consultec Scientific, Inc., submitted a grant application and was subsequently awarded a Special Research Grant to organize and direct a panel of experts to conduct a Research Needs Assessment entitled, "Advanced Heterogeneous Catalysts for Energy Applications". The objectives of this project were to provide an assessment of the direction, content, and priority of research needs over the long term (5 to 20 years) that will provide the best chance for success in achieving enhanced utilization of advanced heterogeneous catalysts for energy related applications. Included are energy conservation through process improvement, uses in alternative fuel development or alternate feedstock utilization, and applications to alleviate pollution from energy processes. Specific examples are heterogeneous catalysts in coal liquefaction, coal gasification, biomass conversion to gaseous and liquid fuels, use of non-petroleum feedstocks in chemicals manufacturing and conversion of natural gas to liquid fuels. The study does not address electrochemical, photochemical, biochemical or homogeneous catalysts.

DISCUSSION OF THE PROBLEM

The need for new and improved technology to meet our energy needs has been articulated in the National Energy Strategy prepared by the DOE in 1991. It is clear that major needs are technology for economical manufacture of transportation fuels from abundant non petroleum sources, for pollution abatement in energy utilization, and technology which would lead to energy conservation. The application of catalysis is believed to have great promise to provide the basis for fulfilling such needs.

Fortunately, there are abundant resources of coal, biomass, and gas in the United States. It is known that these can be transformed to high quality fuels, however, at present such processes produce fuels which are about twice as expensive as petroleum at world prices.

Heterogeneous catalysis has revolutionized petroleum refining and petrochemical manufacture. It is believed that intensive, directed research can lead to appropriate technology applied to alternative feed materials. General guidance has been provided recently by the reports, "Catalysis Looks to the Future", National Research Council, 1992; Coal Liquefaction - A Research and Development Needs Assessment (DOE Panel 1989); and the earlier, "Opportunities for Chemistry", (Primentel Report) National Academy of Science, 1985. However, these only give general guidance. The present study is designed to provide specific up-to-date evaluative assessments and prioritized recommendations.

Great strides have been made in the transformation of catalysis from an art to a science. This assessment of research needs is based on examining a logical progression of catalytic technical areas summarized below:

Catalyst synthesis begins with the design concepts of physical structure and elemental composition, including oxidation states and coordinational and other interactions between catalyst components. The knowledge of and lack of knowledge of metals, ceramics, zeolites and special supports such as membranes was assessed as well as preparational techniques.

Catalyst characterization by the wide array of modern instrumental techniques offers critical insight into catalytic structures on an atomic scale. Some of the techniques that are presently available for characterization include:

> Surface Science: LEED, UPS, XPS, AUGER, SIMS, RIS, SIRIS, XAFS, XANES, XRF, SERS, NMR, Mossbauer, FTIR
>
> Imaging: SEM, TEM, STM, Scanning Auger
>
> Classical: IR, UV, XRD, Raman

These and other characterization technologies were reviewed for applications in catalysis.

Catalysts performance testing strategies in diagnostic experiments and in practical fuel synthesis conditions is expected to be a major consideration. A knowledge of the status of catalytic mechanism determinations is believed to be fundamental to determining research needs and directions. Further, an assessment of an understanding of resistance to deactivation by poisoning or sintering is important since the practical value of a catalyst is often determined by its capability to remain active and selective.

Interpretation of experimental information is critical to catalytic advances. Therefore, this study included a major focus on the status of knowledge and future prospects for a better understanding of catalyst structure/performance relationships and particularly deduction of scientific factors which underlie catalyst activity and selectivity.

Engineering of catalytic processes is often the key to successful operation. This entails the utilization of kinetic and calorimetric information. Reaction modelling and computer reaction design is of growing importance. Successful catalyst application also depends on an appropriate knowledge of mass and heat transfer within catalyst pellets and in reactor systems. It is significant that innovative engineering has been responsible for several of the most important catalytic engineering advances, *e.g.* fluid bed processing.

Catalysts for pollution abatement represent a significant component of this assessment. This includes processes for catalytic conversion of stack-gas pollutants to a harmless form. A prominent example is conversion of NO_x directly to N_2 and O_2. Environmental aspects of catalyst preparation and use can control catalyst acceptability.

Systems evaluations can provide important research guidance by revealing quantitative information on the value of utilizing a catalyst in a particular process. Evaluation of the economics of fuel manufacture and use, as well as the implications of alternative feedstock utilization, were part of this needs assessment.

The overall approach utilized to fulfill the objectives of this assessment, was to address generic catalytic operational elements — catalyst preparation, characterization, performance testing, etc. as discussed above. These elements provide the basis for mutual technologies which are applicable to specific issues, namely, coal and biomass conversion to liquids and gases, flue gas clean-up, use of nonpetroleum feedstocks in chemicals manufacture, and conversion of natural gas to liquid fuels. The panel members are foremost experts in the specific science and technology in these fields, and there are at the forefront in their expertise in state-of-the art catalytic theory and practice. In catalyst synthesis, design follows function. Function, activity, and selectivity are determined by interactive reactant/catalyst chemistry.

Heterogeneous catalysts are recognized to be central to production and consumption of fuels, manufacture and processing of chemical feedstocks and plastics, pollution abatement, and energy conservation. Recent advances in catalytic science and technology have been profound. These give exciting promise for new and greatly improved catalytic technology in national energy applications. It is visualized that benefits can be:

1. Synthetic fuels manufacture which is much more economically attractive (lower plant investment and operating costs).

2. Use of alternative feedstocks available in the United States (gas, coal, biomass).

3. Energy conservation through improved processes which operate with better energy efficiency.

4. Abatement of pollution in fuels processing and use, including fuels which lower tail gas pollution. At present, the use of catalysts to remove pollutants has been stressed. However, we are moving into an era in which catalytic processes are being devised which avoid the formation of pollutants. Examples are use of non-liquid acids for alkylation and use of a combustion catalyst to carry out combustion at lower temperatures (*e.g.* for generation of electricity using turbines, being developed at Catalytica) and so avoid the formation of NO_x.

5. Significant scientific advancement applicable in catalysis and related fields.

Consideration of these factors and an educated estimation of the difficulty and likelihood of success formed the basis of our evaluative process and prioritization of recommendations.

It is believed that there are excellent opportunities for catalytic technology to make major improvements in the long range (5 - 20 years) to our national energy applications. As Antoine de Saint Exupry said in his book, *Wind, Stars, Sea and Sand*", "When it comes to the future, our task is not to foresee it but to enable it to happen."

METHODOLOGY

The assessment was performed for the Department of Energy by an international panel of scientists representing a wide background of experience and expertise necessary to produce a comprehensive and authoritative assessment report.

Dr. Harvel Wright, President of Consultec Scientific, served as Project Manager. Dr. G. Alex Mills, Center for Catalytic Sciences, University of Deleware, served as the Principal Investigator. The remainder of the panel of experts included:

Dr. Russell Chianelli	Exxon Research and Engineering Co.
Dr. Heinz Heinemann	Lawrence Berkeley Laboratory
Professor Henry Foley	University of Deleware
Professor Gary Haller	Yale University
Dr. James E. Lyons	Sun Company
Dr. George Parshall	E. I. Dupont de Nemours & Co.
Dr. Jule Rabo	U.O.P., Inc.
Dr. Jens Rostrup-Nielsen	Haldor Topsoe A/S
Professor Wolfgang Max Hugo Sachtler	Northwestern University
Professor Kenzi Tamaru	Science University of Tokyo

This outstanding team of experts was carefully selected to meet the following criteria:

1. The team provides a broad coverage of the technical areas that are needed for the study. Figure 1 indicates the technical areas which are covered by the panel members.

2. The team contains representatives from both academia and industry.

3. The panel includes experts from Europe and Japan to insure international coverage from these areas.

4. The team is sufficiently broad and diverse that the possible bias of one or more members will not be sufficiently important to produce an undesirable bias in the final report.

Panel members had two responsibilities during this study. First, each panel member was to research a given area and prepare a section of the report. Second, the panel was to prepare and prioritize a list of research needs in the subject area. Twice during the study the full panel held two day long meetings with DOE personnel. The first meeting was concentrated on establishing the objectives and developing the plans for carrying our the study. The second meeting concentrated on the panelists presentation of their respective findings and on establishing and prioritizing the research needs.

A draft of the report of the study was prepared and submitted to a list of peer reviewers for their comments. The peer reviewer comments were then addressed and the final report prepared and submitted for publication. The deliverable product from this assessment is this report representing the findings of the panel of experts. Based on the collective expertise of the experts who have contributed ideas and suggestions during this study, this report stresses recommendations which the panel feels will enable the DOE to focus its research directions and improve its research capabilities over the long term (5 to 20 years).

AREAS OF PANEL EXPERTISE AND EXPERIENCE

CATALYSIS SCIENCE AND TECHNOLOGY	Mills	Chianelli	Foley	Haller	Heinemann	Lyons	Parshall	Rabo	Rostrup-Neilsen	Sachtler	Tamaru
Preparation:											
Rational design - state of art	X	X	X		X	X	X			X	X
Rational design - computer graphics expert systems (A.I.)			X								
Materials science - ceramics, zeolites, other supports, membranes	X	X	X	X	X	X	X	X	X		X
Materials sci. - metals, complexes, compounds	X	X	X	X	X	X	X	X			X
Preparational techniques	X	X	X	X	X	X	X	X			X
Characterizations:											
Surface science: XDR, FTIR, NMR, ESCA, TEM, LEEDS, UPS, EXPS, SIMS, STM		X	X	X	X	X	X	X	X	X	X
Physi-, chemi- sorption areas, pore size distributions	X	X	X	X	X				X	X	X
Performance Testing:											
Methodology, technique, apparatus, Analytical: activity, selectivity	X			X	X	X	X	X	X		X
Mechanism determination, kinetics, isotopic tracers	X			X	X	X	X		X	X	X
Resistance to deactivation, poisons, sintering	X	X		X	X	X	X		X	X	X
Interpretation:											
Structure - support interactions	X	X		X	X	X	X	X	X	X	X
Structure - performance relationships, atomistic, electronic	X	X		X	X	X	X		X	X	X
Engineering:											
Heat, mass transfer issues					X				X		
Innovative reactor design			X		X		X	X	X		

	Mills	Chianelli	Foley	Haller	Heinemann	Lyons	Parshall	Pasbó	Rostrup-Neilsen	Sachtler	Tamaru
Environmental Aspects: Catalysts for abatement	X	X	X	X	X			X	X	X	X
Preparation and use			X	X			X				X
Systems Evaluation: Economic evaluation							X		X		
Supply (coal, gas, biomass) impact					X		X		X	X	
Environmental impact		X		X	X		X		X		X
Overall evaluation	X	X			X		X	X	X	X	
RESEARCH EXPERIENCE											
Academic, Institutional	X		X	X	X	X		X		X	X
Industrial	X	X	X		X	X	X	X	X	X	
APPLICATIONS EXPERIENCE											
Transportation: Fuel supply, fuel use	X	X	X		X	X		X	X	X	
Industrial: Petrochemicals	X	X	X		X	X	X	X	X	X	
Pollution Abatement		X		X	X				X	X	X

Appendix C

GLOSSARY

ACGIH	American Conference of Governmental Hygienists
AGC	Advanced Gas Conversion
AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscope
ALE	Atomic Layer Epitaxy
CAAA	Clean Air Act Amendments
CFCS	Chloro Fluoro Carbons
CFDS	Computational Fluids Dynamics Services
CRGT	Chemically Recuperated Gas Turbine
EELS	Electron Energy Loss Spectroscopy
ESCA	Electron Spectroscopy for Chemical Analysis
ETM	Electron Tunneling Microscope
EXAFS	Extended X-ray Absorption Fine Structure
DIPE	Diisopropyl Ether
FCC	Fluid Catalytic Cracking
FFV	Flexible Fuel Vehicle
FGD	Flue Gas Desulfurization
FT	Fischer-Tropsch
FTIR	Fourier Transform Infra Red
GNP	Gross National Product
HCFCs	Hydrochlorofluorocarbons
HDM	Hydrodemetalization
HDS	Hydrodesulfurization
HFCs	Hydrofluorocarbons
HREEL	High Resolution Electron Energy Loss

IFP	Institute Française du Petrol
IGCC	Integrated Gasification Combined Cycle
IGT	Institute of Gas Technology
IIT	Illinois Institute of Technology
IM	Inspection and Maintenance
ISS	Ion Scattering Spectroscopy
LEED	Low-Energy Electron Diffraction
LNG	Liquid Natural Gas
LPCVD	Low Pressure Chemical Vapor Deposition
LPG	Liquefied Petroleum Gas
LPMEOH	Liquid-Phase Methanol
MAS	Mixed Alcohol Synthesis
MASI	Most Abundant Surface Intermediate
MBE	Molecular Beam Epitaxy
MELS*	Tetravalent Metal Phosphonates
MOGD	Mobil Olefins to Gasoline and Distillates
MTBE	Methyl Tertiary Butyl Ethel
MTG	Methanol-To-Gasoline
MTO	Methanol-To-Olefins
NGL	Natural Gas Liquids
NMHC	Non-Methane Hydrocarbons
NMR	Nuclear Magnetic Resonance
NRC	National Research Council
PETC	Pittsburgh Energy Technology Center
RDS	Rate Determining Step
RITE	Research Institute of Innovative Technology for the Earth
SASOL	South African Coal, Oil, and Gas, Ltd.
SCR	Selective Catalytic Reduction
SMDS	Shell Middle Distillate Synthesis
SNG	Synthetic Natural Gas

SRC	Solvent Refined Coal
STM	Scanning Tunneling Microscope
TBHP	Tert-Butyl Hydroperoxide
TIGAS	Topsøe Integrated Gasoline Synthesis
TPD	Temperature Programmed Desorption
TPR	Temperature Programmed Reduction
TVA	Tennessee Valley Authority
VOCs	Volatile Organic Compounds
XANES	X-ray Absorption Near-Edge Structure
XPS	X-Ray Photoelectron Spectroscopy
ZSM	Zeolite Synthetic Mobil
Nanoscale	molecular scale. 1 nanometer = 10^{-9} meter = 10Å
Heuristic	rules assembled through experience (rather than theory)