

PREFACE

Coal-derived transportation fuels can be generated by direct liquefaction, involving high-pressure hydrogenation of coal to liquid hydrocarbons, and by indirect liquefaction, which first converts coal to syngas and then upgrades the syngas to motor fuels. Of these two schemes, indirect liquefaction - specifically, the syngas-conversion route - is more susceptible to advances arising from new catalyst developments. It is in this area of catalytic conversion of syngas to transportation fuels that the work described in this report has been directed.

The addition of light alcohols produced from syngas to petroleum-based motor fuels offers this country an economic solution in moving toward energy self-sufficiency. The fuel-alcohol market is developing with the growing use of methanol and ethanol in gasoline; since these alcohols can be produced from almost any carbonaceous source - including coal - the expansion of their use offers a feasible and economic approach to reducing our dependence on foreign petroleum sources.

The utilization of alcohols in gasoline is a commercial reality today. Alcohols presently being used in transportation fuels are fermentation ethanol, methanol, and the butanols. The major reasons for the significant penetration of these alcohols into the fuels market are:

- The lowering of lead content in gasoline has required alternative means of increasing the octane ratings of this fuel. The light alcohols methanol and ethanol have very high blending octane ratings, and offer an inexpensive route to high-quality gasoline.
- Methanol and ethanol can be produced from domestic non-petroleum resources. Coal-to-methanol manufacturing technology via synthesis gas is well-established, and a large fermentation ethanol capacity is now in place.

- Gasoline-ethanol blends and gasoline-methanol blends with higher alcohols (such as butanol) as cosolvents have been shown to be viable and practical fuels for existing gasoline engines.

Gasoline blends which contain 10 volume percent anhydrous fermentation ethanol ("gasohol") possess acceptable water tolerance, volatility, materials compatibility, and excellent octane quality (the (R+M)/2 rating is about three points higher than that of the base gasoline). Therefore, from a performance standpoint, ethanol is a good extender for gasoline. However, the economics of fermentation ethanol are such that it can be competitive only with the aid of both federal and state tax exemptions.

Gasoline-methanol blends must contain a higher alcohol such as butanol to have satisfactory water tolerance and volatility. Both the performance characteristics and economics of methanol-containing blends depend on the concentration of methanol present as well as the methanol/higher alcohol ratio employed.

We believe that the current utilization mode of alcohols as gasoline extenders does not fully realize their economic and performance potential as fuel components. Our extensive experience with gasoline-alcohol blends indicates that the most effective alcohol extenders in terms of performance are mixtures of lower and higher alcohols. The lower alcohols, i.e., methanol and ethanol, should constitute the major portion of the mixed alcohols and will provide the much-needed octane improvement. The higher alcohols, i.e., alcohols in the C₃ to C₅ range, are needed to provide water tolerance and volatility control. An optimum mixed-alcohol fuel extender would have a C₁-C₂ to C₃-C₅ ratio in the range of 2.3 to 4.0 with the distribution of higher alcohols centered on the C₄ alcohols. It was the objective of this program to develop novel homogeneous catalytic systems capable of producing, from coal-derived syngas under attractive process conditions, a suitable product mixture for this optimum alcohol fuel extender.

Although much effort has been directed over the past five decades toward the conversion of syngas to hydrocarbons, much less attention has been given to the production of alcohols. Nevertheless, processes forming alcohols could have significant advantages over hydrocarbon-forming reactions.

One limitation of the Fischer-Tropsch reaction, which produces hydrocarbons, is the statistically controlled product distributions. The result is that a broad range of products is formed, as described by an Anderson-Schulz-Flory analysis. The lighter products which are necessarily formed are not liquids and have little use as transportation fuels; thus they represent an inefficiency in the process. Heavier products, such as waxes, must be cracked to convert them to useful fuel products, and are also a problem to separate from the catalyst.

The production of alcohols can potentially overcome these problems. Alcohols are not necessarily formed by a polymerization process on the catalyst surface; thus they may not be produced in a statistical distribution. Indeed, many examples are known of alcohol product distributions which sharply deviate from the statistical prediction. Furthermore, light alcohols, unlike the light hydrocarbons, are liquids and are quite useful themselves as transportation fuels. Thus the product distribution can be centered on the low molecular weight products to avoid production of the troublesome high-boiling compounds.

Many of the known alcohol-producing catalysts are also good water-gas shift catalysts. This property would have an advantage for the use of low H_2/CO ratio syngas, since the oxygenated by-product can then be carbon dioxide rather than water. The result is that hydrogen is not consumed in formation of the stoichiometric by-product, but surplus CO is utilized instead. A substantially lower syngas ratio can thus be efficiently utilized for the production of alcohol products.

Another advantage of a program which focuses on alcohol production is the potential for the use of homogeneous catalysts. These catalysts have been shown to have many benefits over heterogeneous catalysts in various types of processes. They have also been found to have potential for

the efficient production of alcohols from syngas, but do not seem to be suitable for hydrocarbon production.

Among the advantages of homogeneously catalyzed processes are:

- the excellent temperature control and efficient removal of heat from the liquid phase in highly exothermic syngas conversion processes,
- the possibility of high conversions and reduced recycle costs, and
- the elimination of solids handling problems inherent in slurry-phase operation of heterogeneous catalysts in the liquid phase.

In addition to these process advantages, homogeneous catalysts generally operate under less severe temperature and pressure conditions. Lower reaction temperatures may result in greater selectivity to the desired products, and lower pressures permit decreased investment and operating costs. Homogeneous catalysts also exhibit higher specific activity and can remain active longer because of the absence of surface phenomena.

Because of the potential advantages of homogeneous catalysts, the possible catalytic advantages for alcohol synthesis, and the probable future needs for such alcohols as fuel extenders, the research described in this report has been directed specifically toward the formation of alcohol products by homogeneous catalysts.

1.0 CONTRACT OBJECTIVE

The objective of this contract was to develop and evaluate novel homogeneous catalytic systems for the selective conversion of synthesis gas to alcohol fuel extenders. This was to be done through extensions of known catalyst systems and by design of novel systems. The characteristics of these catalysts which affect their performance in alcohol synthesis -- selectivity, activity, and stability -- were to be evaluated, and fundamental catalyst chemistry involved in syngas conversion to alcohols was to be studied.

2.0 ORGANIZATION

This contract for the study of alcohol production for fuels from syngas by homogeneous catalysts was conducted in the Central Research and Development Department of the Engineering, Manufacturing, and Technology Services Division of Union Carbide Corporation.

The work was performed at Union Carbide Corporation's South Charleston Technical Center, South Charleston, West Virginia 25303.

Principal investigator was Dr. B. Duane Dombek.

Program manager for the first year of the contract was Dr. David L. McKinley. Program manager for the remainder of the contract was Dr. Don C. Best.

Experimental work was conducted by the researchers identified below. Experiments have been assigned reference numbers of the form SGHAM-X-#, where the character X identifies the appropriate researcher and # identifies the number of the experiment.

B	D. C. Busby
G	S. L. Gipson
KGM	K. G. Moley
L	T. W. Leung
M	D. S. Miller
REM	R. E. Murray
V	J. L. Vidal
W	R. W. Wegman

3.0 EXECUTIVE SUMMARY

3.1 Goals and Approaches

When this project began, little was known about homogeneous catalytic systems which could produce higher alcohols or mixtures of methanol and higher alcohols from synthesis gas. Relatively few homogeneous systems for syngas conversion were known, and these in general yielded mainly methanol and little of the higher alcohol products. Our plan was to conduct a broad investigation of potential catalytic systems for syngas conversion, and to focus especially on those which seemed to have potential for producing the alcohols ethanol, propanol, and butanol.

As general guidelines, we hoped to find catalytic systems which could produce mixtures of methanol containing at least 30% higher alcohols, with a 90% selectivity to alcohols among the liquid products. These systems should operate at pressures below 6000 psi, with lower pressures being most preferable. Rates to alcohol products of 2.0 moles/liter of solution/hr or greater would indicate that the systems might have practical potential.

We planned a three-task approach in this project. Task 1 was the investigation of ruthenium-based catalysts for syngas conversion. These catalysts appeared to have the most potential for further studies based on our previous experience. Included in this task were studies of methanol homologation, since it is probable that the higher alcohols are formed by this mechanism even in direct syngas conversion systems. Under Task 2 we planned to pursue a variety of novel potential catalytic systems, based on new ideas and approaches from the literature. Later in the project, Task 3 was to be the further study of the most promising catalyst systems found in Tasks 1 and 2.

3.2 Task 1 -- Investigation of Ruthenium Catalysts

Certain soluble ruthenium species, in combination with iodide promoters, catalyze the conversion of H_2/CO into methanol. A small amount of work prior to the initiation of this contract indicated that significant amounts of higher alcohols (ethanol, propanols, and butanols) could be produced under certain conditions. Research in Task 1 of this contract has attempted to more fully explore the potential of modified ruthenium catalysts for the production of mixed alcohol products from syngas, particularly at pressures below 6000 psi, and preferably at pressures from 1000 to 3000 psi.

Ruthenium Catalysts for Direct Syngas Conversion

Prior to the initiation of this contract, it was discovered that the addition of specific lanthanide metal complexes to the ruthenium catalyst significantly increased the overall catalytic activity and the selectivity to C_2+ alcohols. During this contract we have investigated several aspects of these lanthanide-promoted catalysts with respect to the conversion of H_2/CO into mixed alcohols. We have investigated the effects of total iodide concentration, acidity, and solvent polarity on activity and selectivity.

A study of product distribution as a function of H_2/CO conversion (i.e., reaction time) indicated that it is likely that the higher alcohol products are being formed from methanol by a homologation mechanism. The relative selectivity to higher alcohols increased relative to methanol at the longer reaction times.

With the lanthanide-promoted catalysts, we have observed total ROH rates of up to 1.6 mol/l/hr and C_2+ selectivities over 80 weight % (i.e., more than 80% of the alcohol product is alcohols higher than methanol). Typically, carbon selectivities to alcohols (relative to all liquid products) are in excess of 95%. The major

gaseous products are methane and carbon dioxide. These products are generally formed in roughly equivalent amounts and usually constitute 30 to 50% (on a product mole basis) of all reaction products. Except for relatively low rates at these reaction conditions (6000 psi, 230°C), these results were encouraging, so continued studies of these and other ruthenium catalysts were conducted with the goal of further improving the rate.

Experiments were carried out in several novel solvents. Although good catalyst stability and alcohol productivity were seen, solvent degradation was found to be a problem. The use of Lewis acids in combination with these catalyst systems showed in some cases a shift in product selectivity, but again solvent stability was less than desirable.

The effects of using phosphonium halides as solvents were studied during the contract. Some of these materials are molten at reaction temperatures and therefore appear to be suitable solvents. Experiments have been carried out with various additives in these solvents which improve the rate and/or selectivity to higher alcohols. Use of novel additives in tetrabutylphosphonium bromide solvent gives good rates to alcohols (ca. 1.2 M/hr), but the selectivity to alcohols in the liquid product (56 wt.%) is not as good as in NMP solvent. In NMP solvent, this number is typically above 80 wt.%.

Several novel additives, members of a family of metal complexes, were identified which significantly alter the selectivity and/or the activity of the basic iodide-promoted catalytic system. One of these additives substantially enhances the activity of the basic iodide-promoted system in NMP solvent, and at the same time increases the C₂+ alcohol fraction from 10 to 80 wt.%. Most interesting is the observation that some of these additives allow the formation of alcohol products at good rates under significantly lower pressures than previously observed; substantial activity is observed at 3000 psi of syngas pressure. Other related additives have been tested which change the selectivity to higher alcohols without affecting the total reaction

rate significantly.

Continued investigation of this class of additives demonstrated that a number of similar additives have similar catalytic characteristics. A particular additive was found to increase the production of n-propanol, especially in the molten phosphonium salt system. Furthermore, it was demonstrated that the addition of synthetic precursors of one of these additives gave catalytic effects very similar to those of the additive itself. This led to studies on a related class of organic catalyst additives. It has been discovered that one member of this class has the ability to substantially increase the syngas conversion activity of the ruthenium catalyst in several types of organic solvents. A rate to methanol of 2.2 M/hr was observed at a pressure of 6000 psi. The system with this modification is reasonably active even at pressures as low as 3000 psi. Although this particular system does not yield C₂+ alcohols (methanol is the major product), additional additives or cocatalysts have been found to enhance the formation of ethanol. It is presumed that the addition of these latter compounds forms a homologation catalyst system so that some of the methanol produced from syngas is transformed to ethanol in a second reaction step.

We have studied several solvents for this additive-modified system, and have found that the polar solvent sulfolane gives good rates to alcohols, including C₂+ alcohols. This system is also very selective for producing only alcohols. Unlike systems previously described which involve the use of certain metal-containing additives, this system produces only small amounts of other oxygenates such as acetate esters. Furthermore, the rate of formation of C₂+ alcohols is very respectable. For example, at 5000 psi, the rate to C₂+ alcohols is 1.4 M/h with a molar selectivity to C₂+ alcohol of 60%; methanol is the other product and the rate of its formation is 0.94 M/h.

Because of potential drawbacks of sulfolane solvent, such as cost and possible decomposition, other solvents were also tested. Tetrahydrofuran (THF) appeared to give encouraging results. At

5000 psi, a total rate to alcohols of 3.4 mol/l/hr was observed, and 29% of the alcohols fraction was C₂+ alcohols. The yield of other oxygenates was low, at about 8 wt.% of the liquid product. Experiments in alcohol solvents are most interesting. Methanol solvent gave quite good activity, although a net loss in methanol was observed. This apparently results from homologation of a substantial amount of this alcohol to ethanol and higher alcohols. Ethanol solvent has also given encouraging results. At 5000 psi, a total alcohol rate of 3.1 mol/l/hr was achieved, and 31% of the alcohol fraction was C₂+ alcohols. Only 4 wt.% of the liquid product was other oxygenates. These results indicate that alcohols themselves may be the best solvents for these reactions. By recycling the light alcohols methanol and ethanol to the reaction, the yield of higher alcohols could be substantially enhanced.

Ruthenium Catalysts for Methanol Homologation

A ruthenium-containing catalyst system was discovered in Task 1 research which converts methanol to ethanol upon reaction with syngas at very low pressures and temperatures -- 950 psi and 140°C. For the first time homologation of methanol can be effectively carried out at reaction pressures less than 1000 psig. The activity and selectivity are strongly dependent on the catalyst additives utilized.

The importance of having each of four catalyst components present during the reactions has been demonstrated, and the effects of reaction temperature have been explored. Lower temperatures have a significant effect on increasing the selectivity to ethanol. Selectivities to ethanol of 80% and rates above 2 M/hr have been observed; these are close to the best reported for the standard Co-Ru-I catalyst (rate of 4 M/hr, selectivity of 85%) which requires high temperature-high pressure operation (180°C, 4000-8000 psi). Turnover frequencies for the new catalyst are in the range of 20 to 40 moles ethanol per g-atom Ru per hour. Studies of this catalyst were continued under Task 3 of this contract.

3.3 Task 2 - Development of Novel Catalysts

The goal of Task 2 was to develop novel catalysts for the conversion of synthesis gas to higher mixed alcohols. Some of the systems investigated were based on metals not previously known to exhibit significant activity in homogeneous syngas conversion reactions. Other systems investigated involved metals previously known to have syngas conversion activity, but a new approach was pursued to gain activity or selectivity to the desired alcohol products.

Cobalt Catalysts

Investigations of cobalt catalysts have been conducted, with the effort concentrating on identifying suitable solvents to enhance the production of higher alcohols from syngas. Earlier work on homogeneous cobalt systems reported in the literature shows that cobalt catalysts can produce alcohol products, but rates are very low under practical conditions. A number of solvents have been studied, some in combination with additional promoters.

These studies of cobalt catalysts in the novel solvents indicated that it was possible to improve cobalt stability, which allowed the catalyst to remain active for longer periods of time and under a wider range of conditions. However, solvent decomposition was found to be a critical problem. The use of selected catalyst additives to counter this decomposition was not successful. Related experiments with rhodium catalysts showed good solvent stability in some cases, but catalyst activity was low.

Various cobalt complexes were also tested as catalyst precursors in attempts to produce a more stable catalyst. Although some alcohol product was formed under relatively mild conditions, spectroscopic studies after catalysis indicated that the initial complexes had decomposed.

Copper Catalysts

It had been previously reported that various copper compounds in the presence of base are able to catalyze the conversion of H_2/CO into methanol and methyl formate under relatively mild conditions, 80-120°C and 500-2000 psi syngas. In our experience, this catalyst system produced a mixture of oxygenates at rates of about 1.5 mol/l/hr under these conditions. About half of the mixture was methanol, and no higher alcohols were observed.

Prior to the initiation of work on this contract, we found that the inclusion of various additives in this copper/base system produced substantial effects on the rate of the reaction. Rates to oxygenates of higher than 3 mol/l/hr had been observed in these modified systems. Again, about half of the product mixture was methanol, and no higher alcohols were observed. During this contract, we have studied the use of a range of conditions, solvents, and additives with the copper/sodium methoxide system to determine the most active catalyst. We have also studied the effect of several forms of copper and the use of various bases. The goal of this research has been to increase the catalytic activity and to alter the selectivity to produce higher alcohols.

Experiments were conducted using various different solvents and additives in an attempt to extend the lifetime of the catalyst and/or shift its selectivity. Some new products, including ethanol, have been observed in small amounts. However, no significant improvements in lifetime or product distribution were observed.

Experiments have also been conducted to determine how the products are formed in this system. One plausible route is the formation of a formaldehyde or formaldehyde-like intermediate. The other possibility involves hydrogenolysis of intermediate methyl formate to form methanol. Since attempts to trap a formaldehyde intermediate with amines were unsuccessful, it seems unlikely that much free formaldehyde is formed in this system.

Addition of methyl formate to the copper catalyst under

hydrogen demonstrated that this catalyst could hydrogenate the formate, suggesting that this is the catalytic pathway to the methanol product.

Since solids are present in the catalyst solutions following typical runs, an attempt was made to determine whether the catalysis is homogeneous or heterogeneous in nature. Solids were removed via filtration, and both the solids and the filtrates were tested for continued activity alone and with added sodium methoxide. In all cases, no activity remained.

The solids have been examined and found to contain sodium formate and probably copper metal. Similar solids obtained by reaction of copper(I) iodide and sodium methoxide at 100°C under one atmosphere syngas still contain methoxide rather than formate, are highly air sensitive and display moderate catalytic activity under standard conditions of temperature and pressure. After reaction at higher pressure, the solids no longer contain methoxide, but contain instead formate, and are no longer active. The unreactive solids contain copper metal, but work with cupric methoxide has shown that copper metal is probably not the active catalyst, and the actual catalyst is probably a soluble copper complex.

A copper hydride species formed by β -hydride elimination from copper(I) methoxide is believed to be the active copper catalyst species. The reactivity of the complex bis(triphenylphosphine) copper(I) tetrahydroborate in the presence of methoxide as well as the high activity of independently synthesized copper hydride in the presence of methoxide point to the involvement of both a copper hydride species and methoxide in the catalytic system.

Deactivation of the catalyst system seems to be closely tied to loss of methoxide and formation of formate. Water was suspected to play a role in this transformation, but work in carefully dried solvents has demonstrated that water is not the problem.

Because of the practical limitations of this copper catalyst system -- the problems of deactivation and low yields of higher alcohols -- work on this approach was concluded.

Iron Catalysts

An investigation of an electrocatalytic iron-based system reported to produce methanol under very mild conditions casts doubt on the reliability of the literature results. Although a variety of experimental procedures have been investigated, it has not been possible to reproduce the reported production of methanol under one atmosphere of pressure. Serious flaws in the reported experimental procedures and interpretations were found. Experiments carried out under higher pressures with the components of the reported electrocatalytic system also were not successful in syngas conversion. Attempts to use logical extensions of the system have not been found to yield active catalysts under higher syngas pressure.

Other Catalysts

A variety of novel metal complexes and metal complex-solvent combinations have been investigated for their syngas conversion activity. Although some of these systems produced alcohol products, the activities were low in all cases.

3.4 Task 3 - Further Study of Superior Catalysts

Research in Task 3 has been conducted on the novel methanol homologation system which produces ethanol and other products under relatively low pressures. Studies of the catalyst chemistry have been carried out, with an emphasis on the involvement of catalyst additives and precursors in the catalytic chemistry. Investigations have also explored the effects of a number of reaction variables on this catalyst system.

Because of the many variables involved in this methanol homologation system, it was felt that the best approach to gaining an understanding of how each affects the behavior of the system was through statistically designed experiments. These experiments can allow the determination of which variables are most important for obtaining high rates of conversion of methanol to ethanol with high selectivity.

In preparation for the statistically designed sets of experiments to characterize the behavior of the system, the reaction was scaled up from 40 to 150 mL of methanol in a larger autoclave. No problems were encountered, and results analogous to those obtained at the smaller scale were observed.

A first designed set of experiments did not generate data of sufficient quality for quantitative correlations to be made, but did suggest conditions under which a second designed set might be more successful. The second designed set provided excellent quantitative correlations between the variables studied and the rate and selectivity of ethanol production. Unfortunately, the results showed that conditions for highest rate and highest selectivity are mutually exclusive within the range of variables investigated. The highest rate to ethanol is achieved at high temperature and high ruthenium. The highest selectivity requires low temperature.

Several experiments were carried out with added solvents (in addition to the methanol normally used). Although previously

studied cobalt-based homologation systems show increased selectivity with added solvents, experiments with our ruthenium-based system did not result in increased selectivity. However, the reactant methanol may well be the solvent of choice for this reaction.

In the search for further improvements in the new homologation system, research on catalyst additives was continued. Earlier work in this project had shown the importance of specific catalyst additives. Further work was done to attempt to use additives similar to one of these, both to learn about the essential characteristics of this additive and to try to further enhance the rate and selectivity with a different additive. Several more additives of this type have been found to effectively promote the methanol homologation reaction. It appears that we have identified the important factors leading to good additives of this type. With the goal of optimizing the desirable structural and electronic properties of this class of additives, we have developed a general synthetic route to such compounds.

Reactions with the homologation system have frequently been observed to slow during the course of the process. Various factors could be responsible for this observation, including the possibility that this is an artifact of the batch-type reaction when run to high methanol conversions. It has now been found, however, that the use of additional additives of a certain type give a constant rate of gas consumption throughout the reaction. No loss in activity is observed, and in some cases the ethanol selectivity actually increases.

Progress is being made on obtaining patent coverage for this novel catalytic system.

3.5 Conclusions

The concept of using homogeneous catalysts to produce fuel alcohol mixtures from synthesis gas has been demonstrated in this project. A number of novel approaches and ideas were conceived and evaluated experimentally. Significant progress has been made on two approaches to the production of ethanol and higher alcohols; direct conversion of syngas to alcohols with ruthenium catalysts, and the homologation of methanol to ethanol.

Halide-promoted ruthenium catalytic systems were shown to be capable of selectively producing alcohols directly from syngas. In some modifications studied, the fraction of ethanol and higher alcohols in the product was 80% and higher, although the total rates in these cases, being less than 2 mol/l/hr, would require improvement. Other modifications, with certain additives, have recently been found which can produce an alcohol mixture containing 30% of the C₂+ alcohols, and do so at good rates -- 3 mol/l/hr at pressures of 5000 psi. Another attribute of these systems is their good activity in simple, inexpensive solvents such as alcohols. Use of alcohols as solvents can increase the yield of C₂+ alcohols if desired, since recycle of methanol or ethanol to the system leads to their conversion to higher alcohols.

Ethanol is a useful liquid fuel or fuel additive. Previously known methanol homologation catalysts were not active or selective enough to make the homologation route to ethanol feasible. Some of our research was conducted on this reaction, since this process is likely to be involved in direct syngas conversion catalysts which produce ethanol and higher alcohols. In these studies, a novel methanol homologation catalyst was discovered which operates with good rates and selectivities at much lower pressures than previously possible -- typical reaction pressures are below 1000 psi. Rates to ethanol and products which could be easily converted to ethanol of greater than 2 mol/l/hr with selectivities of around 80% are typically observed. Recent results indicate that a class

of promoters has several beneficial effects on the catalyst behavior in this system, including improved stability of the catalyst.

Research on these two approaches to ethanol and higher alcohols will be continued under a new contract, No. DE-AC22-86PC90013. In addition to continued chemical investigations, work under this contract will address the economics of processes based on this technology.

4.0 Experimental Data

4.1 Task 1: Modification of Ruthenium Catalyst System

The approaches followed in Task 1 were largely based on our earlier discoveries of ruthenium-based catalysts which could convert syngas to oxygenated organic compounds with good selectivities. Research under this task has been directed toward further investigation and modification of these systems, and extensions to new ruthenium-based systems. The goal has been to improve the catalyst characteristics at lower pressures, both through catalyst screening studies and through a better understanding of the catalytic process.

4.1.1 Ruthenium Catalysts for Direct Syngas Conversion

4.1.1.1 Introduction

Earlier work at Union Carbide had shown that homogeneous ruthenium catalysts could convert syngas to mixtures of alcohols at significant rates. Work under the contract has therefore pursued related ruthenium-based catalyst systems to study and improve on the characteristics of these catalysts.

Prior to the initiation of this contract, it was discovered that the inclusion of specific lanthanide metal complexes in an iodide-promoted catalyst system significantly increased the overall catalytic activity and the selectivity to C₂+ alcohols. One of the approaches pursued during the contract has therefore been a further investigation of these lanthanide-promoted ruthenium catalysts. The goal of this work has been to improve the activity and higher alcohol selectivity, as well as to investigate the mechanism of this conversion.

Experiments with halide-promoted ruthenium catalysts for direct conversion of syngas to alcohols were also carried out in

several novel solvents. These include various nitrogen-containing compounds, as well as molten phosphonium halides. The use of Lewis acids has also been investigated in combination with these catalyst systems, in an attempt to alter the catalyst selectivity.

Several catalyst additives have been identified which alter the selectivity and/or the activity of the basic iodide-promoted system. Most interesting is the observation that some of these additives allow the formation of alcohol products at good rates under significantly lower pressures than previously observed; substantial activity is observed at 3000 psi of syngas pressure. Some of these additives can also significantly enhance the formation of ethanol and other C₂+ products. It has also been found that it is possible to conduct reactions with these modified systems in alcohols as the solvent, which can have several practical advantages.