VII. COMBINATION SHIFT CONVERSION AND CATALYTIC METHANATION OF SYNTHESIS GAS TO SNG

A. INTRODUCTION

The production of a high BTU gas for use as a substitute natural gas (SNG) involves the catalytic conversion of synthesis gas, CO and H_2, to methane. The synthesis gas is produced by the gasification of coal with O_2 and H_2O in a variety of processes. The composition of this gas is determined by both the coal properties and the conditions encountered during gasification. Typical product gas compositions for several gasification processes are given in Table VII-1. The amount of methane produced varies from 0 to 25%, and is mainly a function of whether the coal is subjected to a low temperature devolatilization step prior to high temperature gasification. The H_2 to CO ratio is generally in the range of 1.5 to 3 although it may be as low as 0.5 as in the and Koppers-Totzek gasifiers due to the high gasification temperature. The sulfur level is dependent mainly on the concentration of sulfur in the raw coal since very little is removed during most gasification processes. An exception is the CO_2 acceptor process of Consolidation Coal Company in which the dolomite, used as a heat carrier, absorbs much of the H_2S and CO_2. The variation in the H_2S concentration in Table VII-1 arises from the use of both western lignites with a sulfur content of less than 1% and eastern bituminous coals with sulfur levels up to 4%.

The exit gas mixture from the gasifier is usually scrubbed clean of contaminants and converted to an optimum composition of CO and H_2 before

TABLE VII-1

COMPOSITION OF EXIT GAS FROM VARIOUS GASIFICATION PROCESSES

Process	Gas Composition (volume %)							Reference
	CO	H_2	CO_2	H_2O	CH_4	H_2S	H_2/CO	
Lurgi (Lurgi Mineraloltechnik G.m.b.h.)	9.2	20.1	14.7	50.2	4.7	(0.3)	2.2	(1)
Koppers-Totzek (Heinrich Koppers G.m.b.h.)	50.4	33.1	5.6	9.6	0	0.3	0.66	(1)
Winkler (Davy Powergas Inc.)	25.7	32.2	15.8	23.1	2.4	0.3	1.3	(1)
Synthane (U. S. Bureau of Mines)	10.5	17.5	18.2	37.1	15.4	0.3	1.7	(1)
Bi-Gas (Bituminous Coal Research Inc.)	22.9	12.7	7.3	48.0	8.1	0.7	0.55	(1)
CO_2 Acceptor (Consolidation Coal Co.)	14.1	44.6	5.5	17.1	17.3	0.03	3.2	(1)
HYGAS: Steam Oxygen (Institute of Gas Technology)	18.0	22.8	18.5	24.4	14.1	0.9	1.3	(2)
HYGAS: Steam-Iron (Institute of Gas Technology)	7.4	22.5	7.1	32.9	26.2	1.5	3.0	(2)

methanation is attempted. The ratio of H_2 to CO is increased to a value near 3 via the water-gas shift reaction, and sulfur as well as other catalyst poisons are removed from the gas stream. It should be noted that sulfur removal may be optionally done before or after the shift conversion, implying a substantial difference in the sulfur tolerance of the shift and methanation catalysts. Current methanation catalysts, generally massive Raney Ni or supported Ni, are extremely sulfur sensitive. Adequate catalyst activity maintenance for these nickel catalysts requires nearly quantitative removal of sulfur. Usual levels of sulfur in the feed stream are between 0.01 and 0.2 ppm. The contribution of the shift, purification, and methanation steps to the cost of the methane produced is estimated to be in the range of 20% (3). Only a small part (~5%) of this is associated with actual catalyst costs. The primary costs are associated with the gasification step. Depending on the process, this can vary between 60 to 80% of the methane value. Process improvements can result, for example, from improved sulfur tolerance and high temperature resistance of the methanation catalyst; the first through less stringent and therefore less costly sulfur removal schemes, and the latter through efficient waste heat recovery at higher temperatures.

In the present section, the focus for process improvements concerning the production of methane will center on two catalytic steps, the water-gas shift reaction and catalytic methanation. The primary problems encountered for these processes and their potential solution by the application of recent developments in catalysis and impacting disciplines will be considered in three parts: short term research, long term research, and supporting basic R & D programs.

B. SUMMARY OF MAJOR PROBLEM AREAS AND CATALYST DEVELOPMENT OBJECTIVES

The problems associated with catalysis of the gas shift and methanation reaction will be divided into three areas, in order of their relative importance: sulfur poisoning, catalyst thermal stability, and carbon deposition. A short discussion will also be included concerning other desirable catalyst properties. Where possible, pilot or laboratory scale test data will be summarized to demonstrate the magnitude of the problem.

1. SULFUR POISONING

The first catalytic process in the conversion of synthesis gas is the water-gas shift reaction. Commercial catalysts for this process include iron oxide-chromium oxide catalysts operating at 315 to 485°C and more active low temperature zinc oxide-copper oxide catalysts (4). The latter catalysts operate in the temeprature range of 175 to 350°C and are very susceptible to low levels of sulfur compounds in the reactant stream. However, the higher temperature iron oxide-chromium oxide catalyst can tolerate H_2S levels of 500-1000 ppm (4). Low temperature operation is preferred because higher equilibrium conversion to H_2 is obtained. For use in hydrocarbon synthesis, total conversion of CO to H_2 is not required, and therefore high temperature, 300-500°C, catalysts are acceptable. Recently, low temperature shift catalysts with significantly increased sulfur tolerance have been developed (5, 6). The data for these catalysts indicate that high levels of sulfur are now not a major problem for the water-gas shift reaction.

Methanation catalysts, on the other hand, are extremely sulfur sensitive. The magnitude of the sulfur poisoning problem can be seen from a calculation of the amount of sulfur needed to deactivate a typical nickel catalyst. The adsorption of sulfur from the reactant stream by Ni is almost quantitative and the sulfided catalyst is inactive for the hydrogenation of carbon monoxide to methane. Deactivation proceeds through the bed as a wave and, for the purpose of this calculation, when 50% of bed is sulfided, it is assumed that the catalyst must be replaced. In reality, the catalyst would probably have to be replaced much sooner than this because of low productivity. Other assumptions are a gas space velocity of 10,000 hr^{-1} and reasonable properties for a high loading Ni/Al_2O_3 catalyst as summarized in Table VII-2. From these assumptions, an estimate can be made of the time required to 1) saturate the Ni surface with sulfur or 2) completely convert the Ni to bulk NiS. At an H_2S level of 10 ppm in the reactant stream, a surface sulfide is formed in five days, and only twenty days are required to completely convert 50% of the Ni to bulk NiS. Only when the level is reduced to the range 1 to 0.1 ppm does the catalyst lifetime become sufficiently long for a practical process.

A level of 1 ppm H_2S in a reactant stream containing 60% (vol/vol) H_2 corresponds to an H_2S/H_2 ratio of 2×10^{-6}. At this H_2S/H_2 ratio, bulk nickel sulfide is not stable at the temperature of operation for most methanation processes (300-450^{o}C) (7). Benard, who has studied extensively the adsorption of sulfur on metal surfaces, has found that a surface sulfide layer on Ni is stable to much lower H_2S/H_2 ratios (8, 9). Comparative data presented by Rostrup-Nielsen at 550^{o}C shows that an H_2S/H_2 ratio of 2×10^{-6} is sufficient to form a saturated sulfur layer on Ni, whereas a ratio of 10^{-3} is required to form the bulk sulfide (10). Thus, the deactivation of Ni by sulfur is probably the result of strong adsorption of H_2S to form a surface sulfide.

Calculated catalyst lifetimes such as that described above can be

TABLE VII-2

EXPECTED CATALYST LIFETIME IN SULFUR CONTAINING STREAMS

PROCESS ASSUMPTIONS

H_2S Concentration	as listed
Gas Space Velocity	10,000 hr^{-1}
Catalyst deactivated at 50% sulfidation	

CATALYST PROPERTIES

Ni Content	25% (wt/wt)
Apparent Bulk Density	1g cc^{-1}
Ni Dispersion(1)	0.25

CALCULATED CATALYST LIFETIME (days)

H_2S Concentration (vol/vol)	Type of Sulfidation	
	Bulk NiS	Surface NiS
10 ppm	20 (days)	5 (days)
1 ppm	200	50
0.1 ppm	2000	500

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(1) Ratio of surface Ni to total Ni present in sample

compared with recent data obtained at Sasol, South Africa in a pilot plant scale methanation operation (11). Using a supported Ni catalyst with a high Ni content, an average level of 0.05 ppm H_2S resulted in slow but noticeable deactivation of the initial portion of the catalyst bed, but no deactivation farther into the catalyst bed even after fifty days on stream. Furthermore, a level of 3 ppm H_2S resulted in very rapid deactivation of the catalyst much further into the catalyst bed after only six days of operation. Operation for 1200 hr. with a sulfur level of 0.05 ppm moved the point of maximum conversion from 20% of the bed length to 22%, while 150 hr. at a level of 3 ppm H_2S moved the maximum conversion point from 22% to 44% of the bed length.

The form of the Ni catalyst does not appear to have a great effect on its sulfur tolerance or sulfur capacity. Similar rapid sulfur poisoning was observed for Raney Ni catalysts in fluidized bed operation (12) or Raney Ni flame sprayed onto tube-wall reactors (13). Sulfur poisoned nickel catalysts apparently cannot be easily regenerated (14). This is probably due to the fact that such regeneration would require one of two practical approaches: reductive regeneration or oxidative regeneration. The former would involve the use of large amounts of costly sulfur free hydrogen or synthesis gas, and may be extremely slow even in pure hydrogen at temperatures as high as 700°C (10). Oxidative regeneration would entail treatment in steam

$$\text{Ni-S} + H_2O \longrightarrow \text{NiO} + H_2S$$

$$H_2S + 2H_2O \longrightarrow SO_2 + 3H_2$$

or calcination in air.

$$\text{Ni-S} + {}^3/2\ O_2 \longrightarrow \text{NiO} + SO_2$$

The first process requires complete conversion to the metal oxide, but does appear to rapidly remove much of the nickel sulfide while the oxygen treatment leads to sulfation of the catalyst and retention of most of the sulfur even at 750°C (10). The oxidation step could have an irreversible adverse effect on the massive nickel catalysts due to interaction of the nickel oxide formed with the alumina support (spinel formation). Regeneration may be possible, however, few data are presently available to suggest that this is the case.

2. OTHER POISONS

The only other poison of consequence is chlorine. Data indicates that low temperature Cu/Zn/Al water-gas shift catalysts are poisoned by the formation of $ZnCl_2$ with resultant sintering of the active copper phase (15). The detrimental level of chloride is much lower than the tolerable sulfur level and, after exposure of the catalyst to chloride, deactivation continues slowly as the active component deteriorates. The chloride is usually introduced from the water supply, and can be prevented from entering the primary reactor by using a guard chamber filled with low temperature water-gas shift catalyst.

3. CATALYST THERMAL STABILITY

A highly exothermic reaction such as methanation can be carried out in two basically different processes. In one, the reaction temperature is kept low by product gas recycle, tube-wall reactor designs, or use of a liquid phase heat removal medium. High catalyst thermal stability is not a prime requirement for such a system. Alternatively, the reactor can be operated without temperature control, i.e. adiabatically, the maximum temperature obtained depending on the conversion limit imposed by equilibrium considerations. In this latter case reaction heat can be extracted at a high temperature improving the overall process thermal efficiency.

At low temperature, both water-gas shift and methanation catalysts maintain activity for extended periods of time in the absence of poisons. Higher temperatures generally result in degraded performance. This is especially a problem for the highly exothermic methanation reaction where the reaction heat can generate very high catalyst bed temperatures. These high temperatures generally result in the loss of surface area of the active component. Pilot plant scale tests of a state-of-the-art high loading supported Ni catalyst (11) employed inlet temperatures of 300°C and exit temperatures of 450°C. These temperatures were not detrimental to overall catalyst performance as shown by measured metal surface areas using specific H_2 adsorption as summarized in Table VII-3. The surface area loss in the high temperature outlet of the catalyst bed is due mainly to hydrothermal sintering of the Ni as shown by the sample treated in H_2 and H_2O only. The catalyst rapidly reaches steady-state and further degradation appears to be negligible. The final methanation reactor operates at lower temperature (approximately 350°C), and is exposed to lower partial pressures of water resulting in reduced catalyst sintering.

Although the temperatures discussed above, 300 to 450°C, give adequate catalytic activity and life, catalysts capable of operation at even higher temperature are desirable. The very large amount of heat released in the exothermic methanation reaction lowers the efficiency of the coal to SNG conversion unless this heat can be recycled for use in the process. The most useful form of heat would be high temperature, high pressure stream. A significant fraction of the methanation heat can be extracted at high temperature by partial conversion of the synthesis gas to methane in a series of reactors operated from high to low temperatures. One

TABLE VII-3

Ni SURFACE AREAS OF SUPPORTED Ni CATALYSTS AFTER PILOT SCALE METHANATION TEST[(a)]

	Ni Surface Area (m^2g^{-1})[(b)]	
Fresh Reduced Catalyst	39.1	
After Treatment with $H_2 + H_2O$	28.0	
From Main Methanation Reactor		
After 1000 hr	15	(Top Bed)[(c)]
	22	(Bottom Bed)
After 4000 hr	14	(Top Bed)
	22	(Bottom Bed)
From Final Methanation Reactor		
After 4000 hr	38	(Middle Bed)

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a. See ref. (11)

b. Calculated from H_2 adsorption assuming 6.5 $Å^2$ per adsorbed H atom

c. Downflow reactor, top is reactor inlet process, proposed by R. M. Parsons Company, operates the first methanation reactors with an outlet temperature of 770°C producing 40 to 50% of the methane at this temperature (16). Heat is extracted between reactors and subsequent reactors, operated at lower temperatures, convert the remaining CO. For this process, catalysts capable of operating at 770°C with possible higher local temperatures are required. Because of the high temperature operation, these catalysts may be less active. Sulfur poisoning is less of a problem at higher temperatures because of the decreased stability of both the bulk and surface sulfide at the conditions of operation.

4. CARBON DEPOSITION

A third major problem area stems from the Boudouard reaction, the disproportionation of CO to CO_2 and carbon.

$$2CO \longrightarrow CO_2 + C \qquad \text{(VII-1)}$$

The other species present in the reactant stream can affect the equilibrium of reaction (VII-1) through the water gas shift reaction (VII-2) or the synthesis of methane (VII-3).

$$H_2O + CO \longrightarrow H_2 + CO_2 \qquad \text{(VII-2)}$$

$$3H_2 + CO \longrightarrow H_2O + CH_4 \qquad \text{(VII-3)}$$

<u>If it is assumed that these reactions proceed to equilibrium</u>, the thermodynamic driving force to produce elemental carbon can be readily calculated for any gas composition from the known free energies of these reactions (17). A particularly useful presentation format is a ternary diagram described by White et al. (18) in which the gas compositions permitting carbon deposition are clearly delineated. For example, a stoichiometric mixture of $3H_2$ + CO will not deposit carbon below a temperature of 430°C at 2 atmospheres pressure. The addition of water further reduces the possibility of carbon formation.

However, the above analysis assumes the species in the reactant stream are at equilibrium, that is, that the reactions (VII-1) to (VII-3) are not kinetically limited. Usually, this is not the case, and therefore these thermodynamic data should be applied with caution. For example, in bench scale tests of Ni catalysts it is generally found that at conditions where carbon is thermodynamically unstable, no carbon deposition is initially observed (18, 19). If, however, a small amount of iron is deposited on the catalyst, severe carbon deposition occurs. This is a direct result of the known activity of reduced iron for the Boudouard reaction and the corresponding kinetically slow gasification reactions. In general, carbon deposition is hindered by establishing a high H_2/CO ratio in the gas phase or by introducing water vapor. Increased H_2 partial pressures shift the equilibrium away from carbon, while the addition of water acts through the water-gas shift reaction to produce H_2 at the surface or by gasification of the deposited carbon. As discussed in Part 1, the steam gasification of carbon is a more rapid reaction than the CO_2 or H_2 gasification of carbon (20).

In acutal use, Ni catalysts operating at temperatures up to 450°C and with 20 to 50 mole percent H_2O in the reactant stream maintain activity for prolonged periods of time when the H_2/CO ratio varies from 5.8 to 2.0 (11). As is the case for sulfur poisoning, catalysts deactivated by carbon deposition reportedly cannot be regenerated (14). However, as mentioned previously for the sulfur-poisoned nickel catalysts, not much systematic work has been published on non-noble metal catalyst regeneration, and therefore under certain circumstances it may not only be feasible, but also practical.

Carbon deposition is generally not a problem in water-gas shift catalysis for several reasons. To drive the reaction toward the formation of H_2, excess water is added which, as shown above, inhibits carbon deposition. This high partial pressure of water also maintains the iron in iron-chromium catalysts in the oxidized state which has very little activity for the Boudouard reaction. As mentioned previously, it is the zero valent iron which is very active for this reaction.

5. SUMMARY

The problem areas described above point to a number of desirable catalyst properties that require development. These are:

1. Sulfur tolerance to a level of 10 to 1000/ppm H_2S
2. Minimal carbon deposition
3. Methanation catalysts which are stable at high temperature operation, i.e. 500 to 800^oC ($1000-1500^oF$)

It should be noted that increased activity or product selectivity are not listed as areas requiring work. Current catalysts possess sufficient activity and in general the selectivity to methane is quite good. However, it is foreseen that sulfur resistant catalysts may in fact be much less active. In this case, activity may become a problem.

C. IMPACTING AREAS AND RECENT RESEARCH DEVELOPMENTS

Application of the developments discussed in Parts 1 and 2 of this study, which are pertinent to the solution of the problems encountered for water-gas shift and methanation catalysis, have been divided into three areas. The first area considers the solution of short term problems, i.e. those which are of primary importance. The second area considers key problems, however, it is apparent that their solution will require greater resources and more time than those in the short term category. Finally, a third area called Supporting Research is included. Programs in this area are of a greater technical and scientific nature than those in the other two areas, and are primarily directed at understanding the basic aspects of the catalytic processes which occur during water-gas shift and methanation.

1. SHORT TERM PROGRAMS

a. Poison Resistant Catalysts

In the search for a catalyst tolerant to the presence of 10 to 1000 ppm H_2S in the reactant stream, it is necessary to use the proper test procedure. In the past, addition of H_2S to integral reactors operating at high conversion gave data more indicative of sulfur capacity. After some arbitrary deterioration of catalytic activity, the test was terminated and the catalyst noted as poisoned. To assess tolerance to sulfur, the activity must be measured after the catalyst has come to steady-state with the H_2S level in the reactant stream. An effective procedure to do this has been described in detail by Dalla Betta et al. (21, 22). Instead of measuring catalyst life in a reactant stream containing 0.1 ppm sulfur, activity of a catalyst saturated with sulfur in an environment of 10 ppm or more H_2S is measured. Data employing this procedure enumerate the importance of variables such as temperature, H_2S concentration, and water vapor.

At low levels of H_2S, 10 to 1000 ppm, bulk sulfidation does not occur on Ni at the temperature generally used in the methanation reaction so that sulfur poisoning is the result of an inactive surface sulfide layer. Thus, the problem becomes one of preventing the formation of this surface sulfide layer. Cluster or alloy formation may alter poisoning effects although this data is very sketchy (23). The requirement is basically that the free energy of formation of the alloy be sufficiently large to inhibit the formation of the surface sulfide from H_2S. Recent data on Ni catalysts in the presence of 10 ppm H_2S show surprisingly high activity for methanation depending on the temperature and the support (21). The cause of this effect is not well established, but may be associated with a surface carbon containing layer that inhibits the formation of the inactive sulfide (22). A carbon layer on Ni is not sufficiently stable to totally exclude sulfide formation since the nature of the support and the presence of water in the reactant stream cause wide variations in the observed sulfur resistance. However, these results demonstrate one approach. The multiplicity of possible metal-support interactions (24) make this an area worthy of investigation. For example, it has been found that the energy of interaction of the metal with the support can be altered by changing the support (25). Metal particle size will also be important, not necessarily because activity is a function of the particle diameter, but because the smaller particle is necessary to maximize interaction with the support and the effects of promotors that are located predominantly on the support. Techniques for the preparation of highly dispersed metals are fairly well developed and have been discussed in some detail (26). Work in this area, however, should be directed to activity measurements in the presence of H_2S under conditions as nearly real as possible since it has been clearly shown that reaction temperature and the presence of water vapor have profound effects.

A second area that may yield short term benefits is catalytic testing of known and characterized materials that may exhibit stability in H_2S. Intermetallic compounds such as $ZrPt_3$ and some of the more common carbides and nitrides should be tested for catalytic activity in the presence of

10 to 1000 ppm H_2S. Nickel boride, for example, has similar hydrogenation activity to Ni (27). The stability of these materials toward sulfidation has been discussed in Part 2 (28). Although not stable in high concentrations of H_2S such as 1%, only partial sulfidation may occur at lower levels.

Catalyst degradation due to carbon deposition suggests a completely different approach. In this case, proper selection of the components of alloy catalysts may give increased hydrogenation activity of the surface while decreasing its tendency to form unsaturated polymeric residues (29). Polymeric acetylenic residues are thought to be coke precursors and require at least three contiguous metal sites for formation (30).

b. Thermally Stable Catalysts

Development of more thermally stable catalysts capable of operation at higher temperatures can be accomplished by stabilizing supported Ni, currently the best candidate as a methanation catalyst, or by developing new catalytic phases that possess high thermal stability. In both approaches some work will be basically short term, involving technology already tested or partially developed for other systems and reactions while other concepts involve more long term research and development, and will be discussed later.

Methanation is carried out in a highly reducing atmosphere, H_2 + CO, and therefore the Ni is in the reduced state. As such, the interaction with the support is small, and as the maximum operation temperature is raised from 450°C to 700-800°C, sintering is expected to be severe. Addition of other compounds to act as structural promotors offers promise. Also, stabilizing the support to high temperature sintering (31) will aid in maintaining the surface area of the supported active component. This includes the use of ultrastable zeolites which have been developed to withstand temperatures up to 800°C in atmospheres containing water vapor (31).

Also, structural promotors have been used on supported Ni catalysts for other reactions to stabilize the Ni surface area, and should be further developed for methanation (31). One example would be the use of transition metal oxides such as Cr_2O_3 (27) to stabilize the surface area of other types of nickel catalysts.

The combination of two metals to form an alloy during operation may offer increased thermal stability. Ruthenium decreases the tendency for copper to sinter when comparing the RuCu cluster with pure supported copper (32). Similar behavior has been noted in other alloy systems (33), and may be used to increase the thermal stability of Ni or, alternatively, to construct other active systems with high thermal stability.

c. Engineering Developments

The highly exothermic nature of the methanation reaction and the low temperature limit beyond which the reaction becomes equilibrium limited have been the driving force for much of the process research in methanation. A number of unusual engineering concepts have, for this reason, been applied to this process. For example, hot and cold product gas recycle was investigated as a technique to limit the maximum adiabatic reaction temperature in both fixed bed and fluid bed reactors. Because large volumes of gas are recycled, pressure drop through the catalyst bed becomes important, leading to the use of tube-wall methanation reactors. The catalytic material employed in this case was Raney Ni alloy flame sprayed onto the tube walls. More recently, monolithic honeycomb ceramic supports have been considered for this particular application. Another engineering concept is the adiabatic operation of the synthesis reactor resulting in very high temperatures, permitting some of the reaction heat to be extracted at high temperature for use as process heat. This particular application has been mentioned earlier with respect to the desire for thermally stable catalysts. Last is liquid phase methanation where use is made of a counter current liquid flow through the catalyst bed to control catalyst temperature. Of these, catalyst coated tube-wall reactors and liquid phase methanation will be discussed in more detail.

The flame sprayed Raney Ni alloy catalysts show very good activity, but suffer from many of the problems of other Ni catalysts, especially poor thermal stability and a lack of sulfur tolerance (34). The thermal stability is aided somewhat by the very good heat transfer properties associated with coating the Ni in a thin layer on a heat exchanger surface. However, this places a limitation on the temperature at which such reactors can be operated and very high throughputs still result in temperature gradients and thermal degradation. Thermally stable and sulfur tolerant materials are desirable and should be developed if the tube-wall reactor is to be more useful. As discussed earlier, composite materials could probably be considered and techniques should be developed to place adherent coatings of these materials on metal surfaces. For operation at very high temperatures, less active materials that are more thermally stable should be considered.

A unique approach to removing the reaction heat is the counter-current liquid phase methanation reactor in which the liquid phase acts as a heat transfer and heat absorbing medium to maintain a low catalyst temperature (35). The advantages of such a system would be efficiency, simple design, and high throughput. However, current tests reveal a relatively low catalytic activity complicated by low reactant accessibility to the catalyst surface due to the presence of the liquid layer (36). If catalyst activity and accessibility can be increased, this system would permit high throughput at a controlled temperature so that the reaction can continue to completion without resorting to heat removal and cleanup methanation.

2. LONG TERM RESEARCH AND DEVELOPMENT

The ideal catalytic system will combine a number of properties including high temperature stability, sulfur tolerance, activity, and good selectivity to methane. However, none of the currently known catalysts for methanation possess both high activity and sulfur tolerance or thermal stability. Therefore, it is likely that new catalytic materials will have to be considered. In this section the primary focus is on understanding the nature of sulfur poisoning, identifying classes of materials which may have desired properties for methanation and water gas shift catalysis, and also on possible procedures for catalyst regeneration. Finally, homogeneous methanation catalysis is discussed because of the possibility of overcoming the sulfur poisoning and heat transfer problems associated with conventional gas phase catalysts.

a. Mechanism of Sulfur Tolerance

Materials resistant to formation of bulk sulfide in the presence of 10 to 1000 ppm H_2S would still be poisoned if a surface sulfide layer forms. However, even this is not known conclusively since few metal sulfides have been tested for catalytic activity. Only Ni and several other metals which are known to be quantitatively poisoned by sulfur have, in effect, been tested. Also, it is not known if partial sulfidation of a catalyst surface will totally deactivate the metal. This latter point is important since to make a metal totally resistant to formation of a surface sulfide will require that the metal be bound strongly to another material. Strong compound formation will probably affect the catalytic activity of the metal and for an active metal like Ni, the effect could be to decrease its catalytic activity. However, this could be tolerable if the catalyst were sulfur tolerant and the activity debit overcome by operation at high temperatures.

The thermodynamics of bulk sulfide formation are, in general, well known. However, very little is known about the chemistry of surface sulfide formation. Only recently have surface techniques such as Auger electron spectroscopy (AES) been applied to bulk metals in the presence of sulfur (8). The extent of surface coverage by sulfur in the H_2S pressure range and H_2S/H_2 ratio of interest here should be compared with the catalytic properties of the surface, or alternatively with corresponding activities measured on supported or high surface area catalysts.

To impart increased resistance to the formation of a surface sulfide layer for a metal will require that the metal be bound to another material. Provided the interaction withdraws electrons from the metal, it is likely that the stronger the interaction, the more resistant the material will be to subsequent sulfide formation. These materials should be characterized, especially with surface sensitive techniques applied in the presence of sulfur bearing gases.

As discussed below, it is desirable to optimize the strength of compound formation since excessive interaction could adversely affect catalytic activity.

b. New Catalytic Materials

An effective catalyst in the presence of sulfur must have activity as well as resistance to sulfidation. Few materials other than the pure transition metals have been tested for methanation. Some of these materials such as platinum, generally not considered as good catalysts for this reaction because of their low activity, may be worthy of consideration due to other properties such as sulfur resistance or high thermal stability (37).

Compound formation to resist surface sulfidation may adversely affect the catalytic activity of the more active catalytic materials. The extent to which this will occur is not known, since few composite materials have been tested for catalytic activity. The synthesis of sulfur tolerant catalysts may then become a compromise in which compound formation is sufficiently strong to prevent sulfide formation, but yet does not destroy methanation activity. The systematic measurement of the catalytic activity of a number of materials such as those described in Part 2, sections II and III of this study (38) would indicate which materials are active for methanation and would define the effect of compound formation on catalytic activity. These same materials could then be studied for surface sulfide formation, both by monitoring catalytic activity and by the use of surface sensitive spectroscopic techniques such as x-ray photoelectron spectroscopy (XPS) or AES as described in Part 2 (39). This will then accomplish the second development requirement, establishing the effect of compound formation on surface sulfide formation. The last step would be the design of a material possessing both activity and sulfur tolerance.

c. Regeneration of Synthesis Catalysts

Very little has been said up to this point about regeneration of methanation catalysts. The reason for this is that attempts to regenerate sulfur-poisoned or carbon-deactivated catalysts have been largely unsuccessful. Generally, this is due to thermal degradation of the catalyst resulting from the high temperatures necessary to decompose the sulfide or to burn off the carbonaceous deposits. Development of catalysts resistant to high temperatures, especially high temperature oxidative regeneration, would then permit use of these catalysts in the presence of sulfur even if poisoned by sulfur. It should be cautioned that the high H_2S levels considered here, 10 to 1000 ppm, would result in extremely short catalyst life. Regeneration cycle times of several days or less could be necessary. Such technology could be readily adapted to fluid bed processing in which the catalyst is continuously regenerated.

d. Homogeneous Methanation Catalysts

Homogeneous catalysts can be readily applied to the CO hydrogenation since the reactants and products are gaseous and separation problems would be minimized. The liquid medium would provide greatly increased heat removal. Also, as discussed previously, there have been suggestions that homogeneous catalysts can be sulfur tolerant although this has not been demonstrated (40). To date, however, no homogeneous organometallic complex has been shown to unambiguously catalyze the hydrogenation of CO to methane. Recently, however, Muetterties and co-workers described osmium and iridium cluster compounds that catalyze the hydrogenation of CO to methane (41). Both $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ at 140^oC and 2 atm total pressure selectively produced methane at a rate of approximately 4×10^{-5} molecules CH_4 per cluster per second (a turnover number, N, of 4×10^{-5} s^{-1}). This compares favorably to the rate measured by Vannice on supported Ir (37). At reaction conditions of 1 atm and extrapolated to 140^oC using the measured activation energy, a rate of 1×10^{-5} s^{-1} is found. Muetterties also found that ligand substitution greatly affected the reaction rate and the product distribution. For example, substitution of triphenyl phosphine for the carbonyl ligands increased the synthesis rate by a factor of approximately 3, but ethane and propane were also produced. An effort was made to establish the homogeneity of the reaction system. These preliminary observations are very encouraging, but the work must be repeated and extended. Certainly, the most interesting aspect of homogeneous catalytic systems is the promise of selectivity control and the possibility for production of specific chemicals from CO and H_2.

3. SUPPORTING RESEARCH

The problems associated with methanation catalysis described above indicate that more basic supporting research would be valuable in three areas. The first of these is understanding the mechanism of CO hydrogenation and the surface properties important to the catalysis. Similarly, understanding the mechanism of sulfur poisoning and the surface properties necessary to inhibit this process is important to the development of sulfur tolerant catalytic materials. Last, the in situ study of catalysts, especially the identification of surface phases during reaction, would be invaluable.

As has been discussed in Part 1, the mechanism of catalytic CO/H_2 synthesis is not well known (42). Current indications are that the reaction proceeds by hydrogenation of a surface enol complex, HCOH, implying the need for good hydrogenation activity. If C-O bond breaking is the rate controlling step, quite different surface properties such as variable surface valence or the formation of a stable surface carbide would be desirable. Such knowledge would facilitate the initial evaluation of catalytic materials.

Recent data (22) show that the activity of a supported Ni catalyst decreases by only a factor of 2 in the presence of 10 ppm H_2S. In the presence of water vapor the activity drops precipitously by 3 orders of magnitude, and is reversible by removing the water vapor from the reactant stream. This behavior is inexplicable at the moment, and may require the use of a technique such as extended x-ray absorption edge fine structure spectroscopy (EXAFS) to characterize the bulk and surface phases present during reaction. For example, in the sulfur tolerance work described above, it is not clear whether in the presence of H_2S the surface has a very low surface coverage by sulfur or even is sulfur free accounting for its high activity. If such is the case, the reason for the inhibition of the formation of the surface sulfide, which should be stable on a zero valent Ni surface at the conditions employed, would be of use in understanding sulfur tolerance. This behavior should be contrasted with the behavior in water-containing streams where the presence of sulfur leads to a totally inactive catalyst.

Characterization of supported catalysts during reaction is a difficult task, but may be a necessity in the case of sulfur poisoning. Electron spectroscopy techniques sensitive to the surface layer, XPS, UPS, AES, etc., all require a high vacuum to permit energy analysis of the emitted electrons. Application to reacting systems, except at very low pressures existing in differentially pumped molecular beam experiments, is impossible. Techniques employing more penetrating radiation such as Mössbauer spectroscopy, infrared spectroscopy, and EXAFS would be applicable to atmospheric pressure and high pressure reaction conditions, but these techniques are in general sensitive to both the bulk and the surface layer. Use of highly dispersed catalytic phases facilitates extraction of surface information making such techniques readily applicable to catalytic problems. In situ study of reacting systems and the development of physical techniques useful in this application should be pursued.

D. CONCLUSIONS

The two primary problems encountered with contemporary methanation and water-gas shift catalysts are sulfur poisoning and thermal instability. Although both reactions can be carried out on a commercial basis, care must be exerted to achieve good activity maintenance. This also means that these processes are not necessarily run under the most efficient and therefore economic conditions. For example, for conventional nickel methanation catalysts the synthesis gas feed must be scrubbed free of sulfur to a level of less than 0.1 ppm. To meet this constraint requires cooling the synthesis gas after it exits the shift reactor (hot scrubbing processes do not remove sulfur to this low level) and re-heating the gas before it enters the methanator. This is thermally inefficient. It would be more economic to use a hot scrubbing process, however, this requires a sulfur tolerant methanation catalyst because this will leave much larger amounts (10 to 1000 ppm) sulfur in the feed gas to the methanator.

Some progress has been made in the development of sulfur tolerant systems. For example, catalyst-support interactions are known to alter the chemical properties of the catalytic phase, sometimes reducing its sensitivity to sulfur. One example of this is the decreased sensitivity to sulfur of nickel on ZrO_2 (21) as compared with nickel on Al_2O_3. The preparation of composite highly dispersed materials by various new catalyst preparative techniques described in Part 1 of this study will be useful in exploring and extending the catalyst-support interaction concept for sulfur tolerance. At low levels of sulfur ($<$ 100 ppm) alloys and the intermetallic compounds developed by materials scientists and inorganic chemists over the past several years may also find application in improving poison resistance. The vast area of new catalytic materials from inorganic chemistry (see Part 1) could have a favorable impact. Many of these novel materials such as the metal cluster oxides (e.g. $Mg_2Mo_3O_8$ which contains Mo_3 clusters) have indicated promise, but have not been studied for methanation or water-gas shift catalysis.

In the short term, experimental leads which have been uncovered over the past several years such as the use of catalyst-support effects, alloys, cluster oxides, and other new materials should be exploited. However, presently there exist few data which give a clear understanding of the nature of sulfur poisoning of metals and oxides. In the long term, a concerted effort will be required to clarify the mode of interaction of sulfur with catalysts and its subsequent effect on surface reactions.

Thermal stability has also been studied in some detail over the last decade, and in many respects substantially more progress has been made in this area than for sulfur poisoning. The nature of the sintering process, while not completely understood in detail, has been modeled for a number of systems so that certain common aspects for various catalysts are apparent. For example, for some materials (e.g. Ru, Pt) sintering occurs in an oxidizing environment by vapor phase transport of an oxidized species (e.g. RuO_4). In this instance, sintering can be controlled by catalyst-support interactions or by forming a surface compound (e.g. $BaRuO_3$). However, much work still remains to be done. In the short term, new preparative techniques in catalysis and the use of metal-support interactions, alloys, and other multicomponent systems will be important for developing thermal resistant catalysts. Recent efforts in steam reforming and catalytic combustion have produced materials which maintain reasonable surface area even at temperatures greater than 2000^oF.

Ultimately, the development of efficient economic methanation and water-gas shift processes will depend upon the appropriate combination of catalytic activity, and especially activity maintenance. The latter factor is influenced by both sulfur poisoning and thermal degradation. However, the contribution of each of these factors is strongly dependent upon the mode of process operation. If the process operates at low temperatures as do most of the present ones, activity maintenance is likely to be affected more by poisoning effects than thermal degradation. However, for high temperature operation, which requires no gas recycle, and leads to greater thermal efficiencies because of the possibility of generating high temperature pressure steam, thermal stability can be more important than sulfur poisoning. Recent work (16) suggests that this later mode of operation may be the more cost-effective for future processes. If this is the case, then increased emphasis should be put on extending catalyst activity maintenance by inhibition of thermal degradation. However, it is abundantly clear that sulfur poisoning will plague methanation and water-gas shift as well as other aspects of synthetic fuel catalysis. Therefore, increased efforts on improving and, in the long run, understanding sulfur poisoning are well warranted.

Finally, engineering improvements, such as trickle bed or fluidized bed liquid phase catalysis (e.g. for methanation) or flame sprayed catalytic tube-wall reactors should be improved. Much of what has been said above as well as the advances in materials science will be helpful in extending these concepts.

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