VIII. Catalysts for the Direct Production of Methane from Coal and Water

The development of a catalyst or a multiple catalyst system for the production of methane directly from coal plus steam was given high priority at the EPRI Conference on "Coal Catalysis." However, this is not included in the EPRI Research Program since the generation of electric power from coal in the absence of cheap and abundant natural methane gas is more easily managed through the production of low-sulfur fuel oil and producer gas of lower energy content. Since the United States possesses an extensive gas pipeline network, the production of methane from coal is of tremendous importance. Therefore, we have included this task in our report, although we have omitted it from the Research Program. The American Gas Association or the National Science Foundation may well want to support this research.

Direct conversion of coal and steam to methane promises to be a reasonably efficient method for producing high BTU gas. Also, techniques learned from this process may enable us to gasify the coal right in the underground seams.

Currently, coal can be transformed into high BTU gas (mainly methane) by use of one of the multi-stage processes now being developed. These processes involve:

1. Production of synthesis gas by coal gasification with steam and oxygen,

$$C + H_2O \rightarrow CO + H_2 \qquad (1)$$

Since reaction (1) is endothermic, oxygen is added to burn some of the coal which provides the heat needed to drive the reaction,

$$2C + O_2 \rightarrow 2\ CO \qquad (2)$$

2. Purification of the gas stream,
3. Adjustment of the H_2:CO ratio to 3:1 by the water gas shift reaction,

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (3)$$

4. Methanation,

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (4)$$

Reaction (1) is endothermic and the equilibrium does not become thermodynamically favorable until the temperature rises above 800°C. Catalysis of this step is discussed in Section III. The water gas shift reaction (3) is slightly exothermic and the equilibrium constant becomes increasingly smaller as the temperature increases. In order to obtain a satisfactory yield of hydrogen, the reaction is usually run below 450°C. Catalysis is important for this reaction. Prior to 1963, shift catalysts contained 70-85% iron oxide promoted with 5-15% chromia. These catalysts were supplemented by a Cu-Zn base catalyst (sometimes containing chromia) which is more active and can be employed at lower temperatures. Even more recently, a spinel-supported Co/Mo catalyst that is resistant to sulfur poisoning and shows high activity at low temperatures has been reported.

Methanation (4) is highly exothermic and is usually run at $\sim 400^{\circ}C$. Nickel is currently the "standard methanation catalyst" and we have discussed methanation catalysts more extensively in Section VI.

The direct production of methane from coal and steam can be considered to be the sum of reactions (1), (2), (3), and (4):

$$C_xH_y + H_2O + O_2 \rightarrow \frac{x}{2}CO_2 + \frac{x}{2}CH_4 \qquad (5)$$

In this overall scheme, the exothermic heat of methanation and partial combustion supplies the endothermic heat of gasification so that the free energy of this reaction is probably favorable at low to intermediate temperatures. The reaction:

$$C_6H_6 + 3H_2O + 3/2\ O_2 \rightarrow 3CO_2 + 3\ CH_4 \qquad (6)$$

is highly favorable at all temperatures, enough so that we can conclude that reaction (5) is probably favorable. Temperature limitations are likely to be those above which methane begins to decompose, $\sim 650^{\circ}C$. Therefore, we probably should not exceed $\sim 550^{\circ}C$ in our attempts to bring about reaction (5).

The combination of gasification and methanation in the same reactor is being studied by the National Resources Research Institute at the University of Wyoming. They hold a patent (U. S. Patent #3,505,204) on a coal-conversion process that employs K_2CO_3 or Na_2CO_3 and Ni as multiple catalysts in a single-stage converter to synthesize methane at $\sim 650^{\circ}C$. By choosing the proper catalyst combination, the conversion can be directed toward the production of hydrogen or liquids or gaseous hydrocarbons. With nickel-alkali, gaseous hydrocarbons are produced, while iron-alkali catalyzes the production of liquid hydrocarbons. Their research is still in the laboratory stage and is currently proceeding with a small-scale ($\sim$100 g coal/run) reactor.

Recommendations

There are currently two large problems associated with finding and developing catalysts for a direct conversion process:

1. Sensitivity of likely catalysts to sulfur poisoning.
2. Transport difficulties in bringing together the coal and the catalyst or catalysts (discussed in Section III).

Since the conventional transition metal catalysts (like Ni) that are used now are easily poisoned by the sulfur present in the coal ($3Ni + 2H_2S \rightarrow Ni_3S_2 + 2H_2$), ways to avoid deactivation must be developed. Some tentative solutions are:

a. Sulfur scavengers
b. *in situo* catalyst regeneration
c. Prior sulfur removal
d. Active, sulfur-resistant catalysts

If an active, sulfur-insensitive catalyst is found, then the sulfur in the coal will present little problem. It will be converted to H_2S in the process which can then be removed from the methane product to an acceptable level with a hot-carbonate scrubber. This is the most desirable of the four alternatives.

W. Wiser and A. Oblad suggest the following generalized reactions for initial fundamental studies on the direct conversion:

1. Carbon and steam
2. Carbon, steam, and oxygen
3. Aromatics and steam
4. Aromatics, steam, and oxygen
5. Carbon and steam modified by presence of $CO + H_2$
6. Aromatics and steam modified by presence of $CO + H_2$

They recommend exploratory research to develop catalyst systems for the reactions indicated. After these systems have been developed, basic research to determine the mechanism of the reactions should follow. The objective is to gain understanding of the reactions between coal, steam, and oxygen. "Only then will practical possibilities emerge."

An alternative, although not quite so direct, path to high methane yield from coal is believed to be worthy of consideration by W. Wiser and A. Oblad. This second path depends upon an economically attractive approach to hydrogen production, probably from char and steam. Development of coal liquefaction technology depends heavily upon an economical hydrogen source and such development is well underway. Coal gasification processes should be prepared to benefit from the anticipated hydrogen production technology.

It is envisaged that one could catalytically hydrogenate a slurry of coal and an appropriate catalyst in a coal-derived liquid, in the temperature range 350-450°C, to produce a liquid, perhaps similar to the liquid of the Synthoil process of the U. S. Bureau of Mines. By combination of thermal and catalytic hydrogenolysis, this liquid could be hydrogenated to a high-methane gas.

The parameters requiring definition and optimization would include:

1. Temperature
2. Catalyst types
3. Pressures
4. Coal/oil/catalyst ratios in slurry

A follow-on program for research would be directed at discerning the mechanisms of the various reactions to enable and ensure optimization of the process.

Bibliography

1. E. J. Hoffman, J. L. Cox, R. W. Hoffman, J. A. Roberts, and W. G. Willson, "Behavior of Nickel Methanation Catalysts in Coal-Steam Reactions." Preprints, Div. Fuel Chem., ACS, 16(2), 64-67 (1972).

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IX. General Guides

It is important to arrive at comparison procedures for candidate catalysts. The specific activity per unit surface area must be used together with a criterion for attainable specific surface areas and surface stability during use. Poisoning effects, cost, and availability must also be considered. Certainly, engineering considerations are also important. It has not yet been possible to put all these considerations together into a single figure of merit, but, hopefully, such useful overall concepts will emerge from the Research Program itself.

Throughout the more basic parts of the Research Program, we recommend the use of the most powerful research tools now available for elucidating mechanisms, e.g., isotopic labeling and tracing, modern electronic surface analysis techniques, and surface area measurements using both BET and chemisorption when appropriate.

Carbides, nitrides, borides, and sulfides of the transition metal elements appear to be relatively unexplored good candidates for new sulfur-resistant catalytic materials, if they can be prepared with high-surface areas. Recently, some new factors have revitalized the traditional approach to the development of catalytic materials. Success has been reported in the preparation of very small alloy particles (with surface areas >100 meters^2/gram) which are in the highly dispersed state necessary for high catalytic activity. Also, it is now possible to measure alloy surface composition by Auger electron spectroscopy and to investigate its electronic structure with ultraviolet photo-electron spectroscopy. Another new technique developed for determining the chemical states and electronic environments of the atomic species is called extended x-ray absorption fine structure (EXAFS) and is based on the analysis of the high-energy side of x-ray absorption edges. Thus, progress in the development of new catalytic materials can be expected to take place due to the improved instrumentation and experimental techniques for synthesis and structure determination.

In order to develop the new catalysts needed, work should be undertaken on the synthesis of promising compounds in extremely fine particle sizes. These and bulk samples should be studied with regard to their compositional, configurational, and electronic structure by means of a variety of physical techniques. In addition, their adsorption and catalytic behavior with regard to simple model reactions should be evaluated. This includes investigating their selectivity as well as their activity.