GASIFICATION CATALYSIS

by

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1. Motivation for Catalysis of Coal Gasification Reactions

The principal motivation for examining the catalysis of coal gasification with steam is to accomplish the gasification reaction at reduced temperatures, where thermodynamics favors increased methane yields and sharply reduced endothermic heat requirements.

2. Background

Catalytic gasification of coal is an old technology, with patents dating back at least to 1884 (Reference 1 contains a good review of the technology dating up to 1928). Most of the technology was directed towards the production of hydrogen for ammonia synthesis. Carbon, in the form of wood charcoal, lignite and sub-bituminous coals, was intimately mixed or impregnated with alkali or alkaline-earth oxides hydroxides, or carbonates. Gasification temperatures were lowered from 800-900° C for uncatalyzed reactions, to 500-600° C, at which temperature hydrogen and carbon dioxide were the chief products. Catalysts that were known to be effective in promoting the shift reaction were added to the alkali and alkaline earth gasification catalysts and found to be effective; addition of other metal oxides, such as iron oxide, were found to increase hydrogen and decrease carbon monoxide yields. Catalysts that were effective in promoting the methanation reaction (primarily nickel) were added to the gasification catalysts but were poisoned sufficiently rapidly by sulphur that increased methane yields were not observed.

While there has been a reasonable amount of work since these early studies, the conclusions have not substantially changed. The most extensive recent survey of catalysts has been carried out by Haynes, Gasin and Forney of the Bureau of Mines (2). They examined some 35 compounds for catalytic activity by simply mixing the catalysts and coal, and concluded the following:

1. Alkali metal compounds and many other materials such as oxides of iron, calcium, magnesium, and zinc significantly increase the rate of carbon gasification and the production of desirable gases such as methane, hydrogen, and generally carbon monoxide during steam-coal gasification at 850°C and 300 psig.

2. The greatest yield of methane occurred with the use of an insert flame-sprayed Raney nickel catalyst (unactivated), which has a limited life of activity. Significant methane increase resulted from the addition of 5 pct by weight of $LiCO_3$, Pb_3O_4, Fe_3O_4, MgO, and many other materials.

3. The increased gasification resulted whether the extent of coal gasification was small or great.

4. At temperatures above 750°C, catalytic effectiveness decreased with further increase in temperature.

5. Residue from total gasification of coal mixed with potassium compounds still contained a significant concentration of potassium (over 10 pct) and was effective as an additive in increasing production of hydrogen and methane.

Gardner, Wilks and Samuels (3) at Case Western Reserve University have examined the effect of some 20 catalysts, impregnated in coal chars, on the kinetics of gasification reactions, and determined thus far that:

1. While a few selected catalysts are as effective as the alkali metals in promoting enhanced gasification rates, none have been found that are more active.

2. Use of the catalysts singly results in only modest changes in the methane yield.

3. Catalysts are more effective in influencing the relative yields of H_2 and CO and CO_2.

4. Catalyst concentrations below 1% by weight are not particularly effective in promoting increased gasification rates.

Personnel at Bituminous Coal Research Inc. (4) examined the use of sodium carbonate as a catalyst, and determined that:

1. The catalyst resulted in a major increase in rate of gas production; the yield of gas obtained with catalyst in 12 minutes was similar to that obtained without catalyst in 120 minutes.

2. Carbon monoxide is formed as a primary product of uncatalyzed gasification more rapidly than it is consumed in the shift reaction.

3. Formation of methane directly from carbon was not definitely indicated.

The extensive studies of Walker and colleagues at Penn. State on the catalysis of the carbon-carbon dioxide and other gasification reactions is well known and will not be reviewed here (see Reference 5 for a recent review of catalyzed carbon combustion and gasification reactions) except to note that:

1. The chemical state of the catalyst is known to be critically important.

2. For pure carbon, substantial catalytic effects are observed with catalyst concentrations in the parts per million range.

3. Anions play an important role.

4. For even pure carbons - the mechanism of action of catalysts is not understood.

3. Recommended Research Areas

The two principal questions regarding the use of catalysts to effect coal gasification are, first, can a catalyst or catalyst system be found to both promote the gasification rate and enhance methane yield, and second, what is the economic feasibility of application and recovery of the catalysts. Neither of the above questions have simple answers. The coal-catalyst-gaseous environment system is complex, and to get answers will require a coordinated study of all three phases. The recommended research areas are:

a. Catalyst Research

A survey of potential catalysts should be completed. It must be noted that it is not sufficient to obtain enhanced reaction rates. The catalyst must increase methane yields so that the endothermic heat requirements are reduced. The relative amounts of H_2, CO and CO_2 yields are of lesser importance.

Such a study should include:

1) Standard Catalyst

Definition of a "standard catalyst and standard conditions" so that reaction rates of various catalysts may be compared. It is generally not possible or useful to refer catalyst activity to the raw coal or char. A suitable standard catalyst would be K_2CO_3, a catalyst which has recieved the most attention and has been shown to be very effective in enhancing reaction rates.

2) Catalyst Systems

Use of catalyst systems, i.e., dual catalysts where one promotes gasification and another controls relative yield of product gases. This area has received very little attention. In oxidation reactions of purified graphite, synergistic effects have been observed (6). The K_2CO_3-Ni system has been investigated by the personnel at the University of Wyoming (7). High conversions to methane were reported, but it is suspected that the nickel catalyst, which was present in large excess, was being poisoned by the sulphur.

3) Chemical State of Catalyst

The chemical state of the catalyst has been shown to be of critical importance in many of the gasification reactions of carbon, although less known of its importance in steam-coal reactions. In the carbon-carbon dioxide-gasification reaction, for example, it is necessary to keep the catalysts in reduced forms (5). Oxidation state of catalysts can be controlled to some extent by the gaseous environment. The extent to which catalysts form chemical compounds with mineral matter in coal is unknown. The technology for study of chemical state of catalysts is available. For example, tools such as induced electron emission spectroscopy are capable of providing this information, and should be utilized in coal catalysis studies.

4) Effect of Catalyst on Coal Structure

There is limited information on the structure of the structure of coals as a function of fractional conversion in steam gasification reactions. There is even less known as to how the presence of catalysts affect the structure. It has been suggested that adsorption of alkalies by carbon prevents graphitization(8)(9). It is recommended that catalysis studies be coupled with extensive x-ray and electron diffraction and electron microscopy investigations of structure.

5) Catalyst Dispersion

The nature of the contact between catalyst and coal is important. It has been shown by several investigators that impregnation of catalysts is much more effective than simply mixing the catalyst and coal particles (10)(5). It is an interesting problem in catalysis, as one is attempting to catalyze a gas-solid reaction by constructing supported catalyst systems with standard techniques, and then attempting to consume the support. Catalyst distribution should be determined by use of instruments such as electron microprobe analyzers and scanning electron microscopes.

6) Mineral Matter and Catalysis

It is apparent that the mineral matter in coal is responsible for enhanced gasification rates compared to demineralized coal of the same pore structure. Dr. Harold Gluskoter is discussing the role of mineral matter in detail in another section of this report.

b. Coal Related Research

It will be necessary in any study of gasification catalysis to undertake careful characterization of the coal-such as prior treatment, petrographic make-up, mineral content, and surface area and pore structure.

1) Prior Treatment

The history of prior treatment of coals affects the crystal structure of the coal, amount of volatile matter, chemical state of mineral matter and catalysts, surface area and pore structure; thus, the chars will require characterization.

2) Petrography

The behavior of the various macerls has received limited attention for both liquifaction and gasification reactions. Little is known as to how macerls behave in catalyzed gasification reaction. As macerls differ in their physical and chemical properties, a variety of separation processes can be employed for coal benefecation. Gasification behavior of macerls should be included in characterization or mechanistic studies. (Ref. 4 contains the results of one such study and a discussion of benefaction techniques.)

3) Mineral Matter

As mentioned previously, mineral matter certainly accounts for some catalytic effects in gasification reactions. There is an additional complication when impregnated catalysts are involved, as the catalysts can have very different effects on the slagging properties of the ash deposits with subsequent effects on gasification rates.

4) Pore Structure

The effectiveness of catalyst impregnation techniques and gasification behavior will be strongly influenced by the pore structure of coal. There are correlations of pore structure with many properties of coal such as rank, adsorptive capabilities, etc., but virtually nothing is known as to the effect catalysts have on pore structure during gasification.

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