

IV. Catalytic Properties of Coal Minerals and Ashes for Liquefaction and Gasification

In order to characterize coal, we must study both its organic and inorganic components as well as the interactions between them. It is then necessary to follow the change in character of these two phases (and their interaction) as the coal undergoes conversion processes. The goal is to relate character to conversion behavior and to be able to predict and understand what effect changes in operation and catalyst additions will have. The other sections of this report deal mainly with the organic phase of coal. In this section, we will discuss the inorganic phase and some of its interactions with the organic phase. Unfortunately, very little factual data are now available on the effect of the inorganic species on liquefaction or gasification.

Ash is usually a major nuisance in the catalytic processing of coal because it dilutes the catalyst and complicates or prevents the economic recovery of catalyst for re-use or regeneration. The fine particles of the ash are so small that they can plug the pores of a high surface area catalyst. In addition, ash frequently has a high content of reactive alkali or alkaline earth ions which can form fusible slag by reaction with the carrier, or by reaction with other ash components which can then coat the catalyst. One way of counteracting such deactivation is to use large catalyst particles moving in a suspension, which continually abrade or attrits off any ash coating on the surface. Ash suspended in product fuels is also undesirable since

it comes through as dirt or deposits on combustion. These negative effects are so strong that coal conversion processes regularly include preliminary de-ashing as an important step, and processes such as coal liquefaction cite de-ashing as a primary benefit.

The major components of coal ash are the common elements of rocks and soils, present as mineral intrusions in the coal. They are combined in widely varying proportions, as in ordinary dirt, and the effects they may have as catalysts or surface active agents will vary accordingly. The petrographic examination of coals to determine which clays or other minerals are present requires a major effort (Penn State), and unless this has been done, there is no reason to assume that the ash from one coal will be the same as another.

The principal minerals found in coals are clays (alumino-silicates), quartz, various carbonates (Ca, Mg, Fe, Mn), hematite (Fe_2O_3), rutile (TiO_2), and sulfides (almost entirely as pyrite, FeS_2). Other minor and trace elements (As, Sb, Hg, Pb, Ni, Cu, Co) may also be present. It is known that some alumino-silicates at elevated temperatures catalyze organic reactions such as hydrocarbon cracking. However, different cation substitutions lead to greatly varying properties so that the catalytic behavior is difficult to predict.

Work is currently underway by P. H. Given and M. Abdel-Baset at Pennsylvania State University to study the effect of various coal minerals on liquefaction. Coal samples are heated in a steel

vessel with tetralin (partially hydrogenated naphthalene). No catalyst or hydrogen is added, but sufficient hydrogen is transferred from the tetralin to the coal to liquify it. With a number of coals ranging in rank from lignite to high-volatile bituminous, the conversion to liquid product is usually increased by some 10% if the coal is first extracted at 60°C with 2N HCl and then washed with deionized water. The effect apparently is not due to strongly-bound HCl that could not be washed out, since exposure of a coal for 24 hours in a closed vessel to the vapor of concentrated HCl does not change the liquefaction properties. A possible explanation of the effect is that the acid treatment removes metal cations from the exchange sites of the clays and increases their catalytic activity, perhaps for hydrocracking. In addition, it has been found that when the Na^+ ion in lignite is exchanged for Ca^{++} , catalytic hydrogenation decreases. These experiments suggest that ion-exchange may be a facile and feasible technique for adding catalytic agents to coal minerals. Indeed, this may be what happens during catalyst impregnation and such phenomena deserve further study.

There is also some evidence that the rehydrogenation of the solvent (naphthalene to tetralene) may be catalyzed by coal minerals, even though a catalyst is not necessary for the transfer of hydrogen from the solvent to the coal. Further careful study of the role of clay minerals in liquefaction processes is necessary.

A single experiment has been carried out in which lignite was treated with dilute HCl to remove all exchangeable cations and

any soluble salts. A portion of the product was then treated with sodium chloride and enough sodium hydroxide to give a final pH of 8.3; the sodium ion introduced was about 3% by weight of dry coal. On catalytic hydrogenation of the two products, cation-free and sodium-rich, it was found that the conversions to oil were almost equal but the viscosity of the oil from the sodium-rich samples was about one-quarter of that of the oil from the other sample. Moreover, the aromaticity of the asphaltenes from the two samples was markedly different. These observations suggest exciting possibilities for controlling the character of the oil obtained from lignites, and raise important issues relating to the catalytic effects of cations in metal carboxylates. An extensive investigation is called for here, in which similar experiments are made with other lignites and other cations.

It has been found with many lignites that the loss in weight on extraction with dilute HCl is in the range 4-8% which is equivalent to at least 50% of the total mineral matter. It seems unlikely that this weight loss could be entirely due to exchangeable cations, and the presence of soluble salts has been suspected. Clearly, the extract from a number of lignites and subbituminous coals should be analyzed for major cations and ions, and for trace elements. Also, sulfur-containing acids (i.e., H_2SO_4 , H_2S) should be investigated in these leaching experiments since sulfur will be plentiful at any conversion plant.

Recommendations

According to P. H. Given, "It is clearly of importance not only to understand the distribution of the various inorganic species in coals and their associations, but also their fate during conversion processes. The latter aspect must be studied by analyses performed on the catalyst, the solid residue, and the liquid products from the process, including the aqueous phase, and for a few elements perhaps also the gaseous products.

"The fate of inorganic species during conversion is also relevant to the environmental impact of coal liquefaction, and this should be borne in mind during studies related to catalytic effects. Some elements may be more or less easily leached by weathering from the solid residue than would be predicted from their mode of occurrence in the original coal. Other elements may appear in the aqueous discharge or as contaminants in the recovered sulfur. If the oils produced by coal liquefaction are to be used for combined cycle power generation, they must not only have low contents of particulate mineral matter, they must also have contents of certain elements (e.g., Na, K, V) at levels of 1 ppm or less. This provides a further reason for determining inorganic species in the product oils."

We must also study the possibility of adding ash for catalytic effects in various reactions. The Bureau of Mines has found that a Kentucky coal with ~17% ash is the easiest to gasify. Might it then be possible to use this spent ash to catalyze the gasification of other types of coal?

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V. Mechanism of Lewis-Acid Catalysis

A promising new technique for coal liquefaction is hydrocracking using molten ZnCl_2 as a catalyst. Suitable modification of the operating procedures and conditions of the hydrocracking leads to a wide variation in the proportion of the various products. The method is particularly suitable for the direct manufacture of low-sulfur distillate fuel oil or high-octane gasoline. Production of distillate fuel oil consumes the minimum amount of hydrogen and is, therefore, cheaper to synthesize than gasoline. Large amounts of ZnCl_2 catalyst relative to the feed must be used; as much as one pound or more of catalyst per pound of feed. This demand for large quantities of ZnCl_2 makes it necessary to recover and recycle a very large portion of the catalyst used.

A ZnCl_2 hydrocracking process has been developed by the Consolidation Coal Company which has advanced to proposed construction of a one-ton of coal per day development unit. In this process, either bituminous coal extract or subbituminous coal is mixed with ZnCl_2 and slurried in distillate oil (b.p. $>230^\circ\text{C}$). The slurry is then heated to $\sim 465^\circ\text{C}$ under a hydrogen pressure of ~ 4200 psig. Under these conditions, the ZnCl_2 is molten (M. P. = 283°C). During the hydrocracking process, more than 90% of the carbon is hydrogenated and the ZnCl_2 catalyst becomes contaminated with ZnS , $\text{ZnCl}_2 \cdot (\text{NH}_3)_4$ and NH_4Cl that are formed by reaction with the sulfur and nitrogen liberated from the feed. In addition to these inorganic compounds, the catalyst leaving the hydrocracker also

contains residual carbon that cannot be distilled out of the melt. When coal is used instead of coal extract, the catalyst also contains the coal ash.

The ZnCl_2 regeneration comprises removal of the bulk of the impurities and must be accomplished without excessive losses of zinc and chlorine. Since the impurities do not settle out of the ZnCl_2 melt, regeneration cannot be accomplished by simple physical means. The Consolidation process regenerates the catalyst by combusting the whole spent melt in a fluidized bed at $\sim 1000^\circ\text{C}$. This removes the nitrogen, sulfur, and carbon impurities and vaporizes the ZnCl_2 (B. P. = 732°C). Carbon is removed as CO_2 with some CO and sulfur as SO_2 . Ammonia is burned to N_2 and H_2O . The vaporized ZnCl_2 is recondensed and is suitably pure for return to the hydrocracker. About 94% of the ZnCl_2 can be recovered by this method.

Recommendations

Although the ZnCl_2 hydrocracking process is well advanced, very little is known about the mechanisms of coal hydrocracking and Lewis-Acid catalysis.

Research is needed in three areas:

1. Thoroughly investigate ZnCl_2 in a large-scale process. Even though ZnCl_2 has been shown to be an effective hydrocracking catalyst on bench-scale tests, the problems of larger-scale operation must be faced. These include optimizing the process conditions and catalyst recovery operations

in order to define the potential commercial economics of the process. Also, corrosion associated with ZnCl_2 and HCl generated by moisture needs to be investigated as well as quantitative data for the effect of feed composition on the process.

With regard to operating conditions, the effect of hydrogen pressure should be investigated as well as the use of catalyst inhibitors. Qualitatively, the effect of pressure is small within the range of hydrogen partial pressures studied, 1500-3500 psig, but the effect of pressure on the hydrocracking rate has not yet been quantitatively defined. In order to maximize the yield of low-sulfur fuel oil and to minimize hydrogen consumption, one may operate the process at high throughputs, decrease the catalyst/feed ratio or use the catalyst in a partially inhibited form. NH_3 , NH_4Cl , NaCl , and ZnO are effective inhibitors for this purpose. However, quantitative data are lacking and should be obtained.

2. Study the mechanism of hydrocracking.

Data are needed on the mode of activation of the hydrogen and on the kinetics of the reaction. This will be discussed in more detail in Section VII.

3. Develop other Lewis-Acid catalysts.

According to W. A. Bailey, Jr., most of the Lewis-Acid catalysts (ZnCl_2 , ZnI_2 , GaBr_3 , TiI_4 , SbCl_3 , AlCl_3 , SnCl_4 , etc.)

have been investigated for coal liquefaction and the probability of finding one significantly better than those already investigated is small. Nevertheless, a basic study of Lewis-Acid catalysis for coal liquefaction with an emphasis on the catalytic mechanism might be worthwhile although of lower priority.

The use of milder reagents such as phenol plus toluene sulfonic acid has been studied extensively in Japan. This is an effective combination for the depolymerization of coal, and it suggests that Lewis acids much less corrosive than the metal halides might be used to advantage. Ample supplies of SO_2 and SO_3 could be provided at any coal conversion plant, and there are numerous possibilities of interaction with aromatics or phenolic compounds available.

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