

CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION

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Research Scope and Objectives

Thermodynamic considerations indicate that the reaction of carbon and water to produce methane and carbon dioxide is thermally neutral and should proceed at low temperatures. We have used graphite as a carbon source to avoid the possibility that any hydrocarbons formed can be derived from hydrogen in the carbon source. It has been our major objective to understand the mechanisms of the reaction of carbon and water in the presence of alkali hydroxide and to determine whether at different conditions higher hydrocarbons may be formed directly without going through the production of synthesis gas.

Nitrogen-containing polynuclear aromatics are constituents of petroleum as well as shale and coal liquids. Removal of nitrogen is necessary to prevent subsequent catalyst poisoning and for environmental purposes in the use of resulting fuels. It has been one of our objectives to avoid having to hydrogenate the entire multi-ring aromatic to remove nitrogen by hydrocracking. The present program uses homogeneous catalysts of the Wilkinson's catalyst type to carry out selective hydrogenation only in the nitrogen-containing ring.

Description of Research Effort

1. Reaction of Graphite and Water

It has been found that graphite and water can be reacted in the presence of potassium hydroxide and other alkali hydroxides (or carbonates) at temperatures as low as 225°C to produce methane and carbon dioxide. In a series of publications (1), mechanisms for the production of CH₄ from carbon and water, resp. H₂, have been elucidated. More recently, reactions of graphite and water have been carried out at temperatures in the range of about 500°C in a flow reactor. It has been demonstrated that hydrocarbons from C₁₋₆ and mostly of an olefinic nature in the C₂₋₆ range can be produced, using potassium hydroxide as a catalyst. Apparently, both a catalytic and a stoichiometric reaction proceed simultaneously. Water is dissociatively adsorbed, and the hydroxyl reacts with potassium hydroxide and carbon to form a phenolate group. The hydrogen is reacting with additional carbon to form hydrocarbons. The reaction leading to hydrocarbon formation stops when all the potassium present has been converted to phenolate. It can be shown that the total amount of hydrogen plus hydrocarbons formed corresponds to one half-mole of hydrogen (as such, or as hydrocarbons) per mole of potassium hydroxide.

2. Selective Hydrogenation of Polynuclear Nitrogen-Containing Aromatics

We have found that it is possible to hydrogenate polynuclear nitrogen-containing aromatics with 100% selectivity for the nitrogen-containing ring only at very mild conditions such as 100-150°C and 200 psig hydrogen, using rhodium or ruthenium carbonyl catalysts. Wilkinson's catalyst is an excellent example of catalysts that perform well. About eight different nitrogen-containing model compounds have been hydrogenated, and while rates change with the type of compounds used, the selectivity is almost 100%. Thus, quinoline is converted to tetrahydroquinoline and acridine to dihydroacridine, while phenanthrene goes to

dihydrophenantrene. It has further been found that the catalyst can be used in heterogenized form, for instance, attached to a vinyl benzene styrene polymer. Cross-linking of the polymer is important in that the less cross-linked the polymer is, the better it is as a catalyst. It has also been found that the reaction is totally reversible and that in the presence of these catalysts, the partially hydrogenated aromatics form excellent hydrogen donors. The donation of hydrogen can again occur in the presence of the catalyst at very mild conditions far away from any possible retrograde-type reactions.

Future Research

In the graphite reaction with water, work has to be extended to other carbon sources such as chars and coals. Our major objective at this time must be to find ways and means to destroy the phenolate and free potassium for further reaction so as to be able to have a continuous formation of hydrocarbons.

In the hydrogenation of nitrogen-containing polynuclear aromatics, better mechanistic understanding of the role of the catalyst in bonding to the nitrogen compound, and in directing its hydrogenation as well as hydrogen donation is required. Experiments should also be undertaken to catalytically crack partially hydrogenated compounds to remove nitrogen from the molecule.

References:

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