CATALYSIS OF COAL GASIFICATION

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I. Introduction

There has been much research and many publications dealing with catalyzing the gasification of carbon. Probably the most complete review of the subject is a chapter written by Walker and co-workers (1) on "Catalysis of Carbon Gasification". Ironically, perhaps, much of the work in the immediate past has been stimulated by the use of graphite in gas-cooled nuclear reactors and the consequent concern about reducing its gasification rate in a coolant stream. In this brief review the areas which are considered to be of major importance will be discussed and an attempt will be made to relate each area to what the particular situation may be for coal and coal chars.

Before considering catalysis and how gasification rates may be affected by catalysts, it is well to remind ourselves that there are other important factors which can affect gasification rates. First, there are two resistances which must be considered when looking at a heterogeneous gas-solid reaction: diffusional resistance and chemical resistance. In the case of coal and char gasification the role of diffusional resistance of reactants to active sites and products always is a fascinating one in which much effort should be expended. It may be more important than a consideration of catalysis to coal gasification. The reason is that coal is a molecular sieve material where most of the active sites for gasification reactions are located in pores of molecular dimensions. It means little if these active sites are very reactive or if an impurity is nearby to catalyze the reaction if the reactant gas has great difficulty getting to the site, that is, diffusional resistance is high. For this reason this writer feels that gasifiers of the future may well be reacting very finely ground coal in the micron range in entrained beds (or fast fluid bed reactors), with recirculation of any material unreacted per reactor pass practiced. In fact, the more diffusional resistance is reduced by working with finer sized material the more important catalytic considerations become since now the chemical resistance step is significant.

The importance of the diffusional resistance step was emphasized in a striking way by Walker and co-workers who studied the reactivity of coal chars to air (2). Reactivity of the char produced from a low volatile bituminous coal was particularly low even though the sample had an ash content of 5%. It was surmised that its low reactivity was primarily due to the high diffusional resistance for air to penetrate into the interior of the char particles. That is, low volatile coals have an unusually small macro and transitional pore system (the feeder pores) through which gas can diffuse at a reasonably high rate to reach the large surface area in the micropores. It was predicted that for this coal, acid treatment in HCl and HF to remove most of the mineral matter and thereby open up some porosity of large pore size within the particles might, in fact, increase gasification rates -- not decrease them because of loss of catalytic material. Acid treatment reduced the ash content from 5.0 to 1.4%; and, subsequently the gasification rate was tripled.

Another factor is important in determining gasification rates and that is the structure of the coal and coal chars. Coal and coal chars have a trigonally bonded carbon arrangement (planar arrangement) as their main building block. This structure resembles graphite in arrangement, the variances being that the layer planes have no three-dimensional order and are more defective than in graphite. Studies on graphite show that its gasification rate is highly anisotropic with carbon atoms at the edges of planes being much more reactive than those atoms within the planes. In graphite, which has many applications where one wants the gasification rate to be small, every effort is made to reduce the ratio of exposed edge to planar carbon atoms. Conversely in the case of coal chars it would be desirable to maximize the edge to planar carbon atom ratio in order to enhance gasification rates if these rates are controlled by the chemical resistance step. How to maximize active site area when coals are taken to reaction temperatures and pressure is an area which is little understood. What is the effect of heating rate, atmosphere, and soak time at maximum temperature as the coal loses volatiles, changes in crystallite sizes, and the structure becomes more or less crosslinked? This is an area which requires research if an understanding of why char reactivity changes markedly with heating cycle is to be understood. However, this area is again outside the present assignment.

II. Considerations of Catalysis of Coal and Char Gasification

A. Theories of catalysis

There are two main theories of catalysis of the gasification of carbon: the electronic theory and the oxidation-reduction theory. In the electronic theory, it is suggested that different impurities in contact with the carbon may either donate or accept electrons from the carbon. In the case of coals and chars which have many defects to trap π-electrons, the Fermi level is low in the carbon; and, therefore, donation of electrons to the carbon from the impurity is expected to predominate. The addition of electrons to the carbon would be expected, in turn, to change the extent of electronegativity of edge carbon atoms, thereby changing the potential energy configuration of the activated complex between the surface and reactant species, and thereby change the activation energy for the dissociative chemisorption of the reactant species prior to reaction and gasification. This theory has not found much experimental support -- but perhaps gasification results of Allardice and Walker (3) on boronated graphite is at least one piece of evidence to support this theory.

The oxidation-reduction theory appears to be more applicable to explaining gasification results. In fact, this is probably not a good name for the theory. What it recognizes is that for gasification to occur, first the gaseous reactant species must dissociate. It further recognizes that a carbon surface, even edge carbon sites, is not a particularly active surface for dissociation of oxygen, steam, carbon dioxide or hydrogen. The catalyst then presents a surface over which the probability of dissociation of the above species upon their collision is much greater. Once dissociation has occurred, the species can seek out a carbon site and gasify that site. For example, from studies where oxygen atoms are produced in a microwave field it is known that they are highly efficient at gasifying carbon as CO with a very low activation energy. Thus the difference between oxygen, steam and carbon dioxide, on the one hand, and hydrogen, on the other hand, is clearly seen. For the former species, an oxygen atom is produced on dissociation which then leads to a simple interaction with carbon to produce a gaseous species. In the case of hydrogen, a hydrogen atom can highly active catalysts for the $C-O_2$, $C-H_2O$, and $C-CO_2$ reactions (1). But when these catalysts become oxidized, they lose their catalysis activity. Walker and co-workers (1) have shown, for example, that iron can be rapidly deactivated as a catalyst at 850°C for the $C-CO_2$ reaction because of its conversion to Fe_3O_4. The addition of sufficient CO to the gas stream will maintain iron in the metallic state and thereby maintain its high catalytic activity. Carbon monoxide is an accelerator for the catalyzed reaction even though it is an inhibitor for the uncatalyzed $C-CO_2$ reaction. McKee has recently shown the same principle for the $C-H_2O$ reaction with iron (5). In steam, the iron is rapidly oxidized and gasification is not catalyzed. In dry hydrogen at 930°C there is some gasification but the catalyzed $C-H_2$ reaction is still slow. In wet hydrogen, the reaction is very rapid since the hydrogen acts as an accelerator keeping the iron reduced. In the reduced state iron catalyzes strongly the $C-H_2O$ reaction.

The chemical form of the impurity can also be of importance in affecting its physical state in some cases. For example, Mo is a solid but MoO_3 is a liquid at gasification temperatures. In the liquid state Mo is seen to be an improved catalyst (6), apparently since its contact area with the carbon surface is increased. Further, its mobility over the surface becomes significant and this may be a consideration in its extent of catalytic activity.

Another important effect of the chemical form of the catalyst is concerned with possible loss of impurity from the system. Consider boron. B_2O_3 is a liquid of fairly low vapor pressure at gasification conditions. It is not readily lost. However, in an environment containing water it is converted to boric acid which is volatile and will rapidly disappear from the system.

A consideration of the chemical form of impurities under coal gasification conditions is extremely complex. Is the atmosphere oxidizing, reducing, sulfidizing? Does it change with reaction time? Does it change from the inside to the outside of the particle? How important is alloying? That is, many of the trace elements when released from the coal matrix upon gasification are expected to be highly reactive because of their small size (perhaps atomic dimensions). Do they, through solid state reactions, form alloys with iron, for example? If so, what is the effect on catalytic activity of particular impurities?

III. Recommended Research for Catalysis of Coal Gasification

A. Activity of major minerals in coal

Specific activities of the major minerals in coal for the gasification reactions should be examined. Studies would best be done selecting a carbon of high purity, which resembles in structure the porous nature of coal. A PVDC carbon should be particularly good. Finely divided carbon particles would be thoroughly mixed with finely divided mineral matter particles. Are there synergistic effects when minerals are mixed together?

B. Possible changes in chemical form of the minerals

Because it has been shown that the chemical form of the catalyst is important, the stability of important minerals in oxidizing, reducing, and sulfidizing atmospheres should be studied. Also what is the extent of solid state reaction of the various minerals with each other at reaction conditions?

C. Activity to methane cracking

It is know that methane is produced during the devolatilization chemisorb on carbon but cannot gasify it. It is necessary to get additional hydrogen attached to the carbon before gasification is possible. Thus the rate of gasification of carbon by hydrogen would be expected to be low -- and it is.

B. Amount of catalyst

In all catalytic processes the question about what is the optimum amount of catalyst is asked. Available data on the subject for gasification of carbon show that as more catalyst is added, over a wide range, gasification rates increase but that the increase per unit of additional catalyst added becomes less. Rakszawski and Walker consider this effect, for example, for iron catalysis of the C-CO_2 reaction (4). In fact, it would be predicted that gasification rates may go through a maximum with increasing catalyst addition if this leads either to serious sintering of catalyst particles as they come into contact at higher concentrations or to blockage and coverage of the carbon surface. The probability of mineral matter and trace elements in coal being present in optimum amounts as catalysts is expected to be low. It was noted by Walker and co-workers (2), in comparing the effect of removal of mineral matter from coals on their subsequent gasification rates, that extensive reduction of mineral matter had variable effects on reduction in gasification rates. Of course, the effect of changing catalyst concentration on gasification rates is entwined in other variables as will be discussed below.

C. Catalyst particle size

The specific activity of a catalyst is expected to increase with decrease in its particle size, since its specific surface area increases with decrease in particle size. The only possible exceptions to this statement which come to mind is where highly active crystallographic face(s) of the solid decrease(s) in amount with particle size reduction or for very small particles the electronic nature of the surface states is sufficiently perturbed to affect dissociative chemisorption rates. Only limited studies have been performed in this area, to the author's knowledge. Rakszawski and Walker (4) looked at the effect of variation in iron particle size in the case of the C-CO_2 reaction. They clearly show a marked increase in specific catalytic activity of the iron with reduction in particle size from 20μm to 0.5μm and then, particularly, for iron from iron oxalate. In the latter case, the carbon was bathed in an oxalate solution, the oxalate decomposed to the oxide, and then the oxide reduced in hydrogen to the metal. From experiences in the petroleum catalysis area, the iron particles from the oxalate would be expected to be quite small.

Indeed, it is interesting to speculate on the particle size effect in the case of coal minerals and trace elements. What are the particle sizes of the minerals in coal? How much variation is there in particle size with coal rank? Is there any correlation of particle size of minerals associated with particular macerals in the coal? Further, even though the trace elements in coal are, by definition, at a much lower concentration level than the minerals they are expected to be much more finely dispersed and possibly in more intimate contact with the carbon atoms? They could be important catalysts, therefore.

D. Chemical form of catalyst

This is a fascinating area, which has many important implications in catalysis of coal gasification. The chemical form of the catalyst can be of major importance in affecting its catalytic activity for a number of reasons. Consider iron and cobalt. In the metallic state, both are of coal immediately prior to significant gasification. Obviously, it is desirable to maximize methane yield, but it is suspected that methane produced within the pore system cracks to some extent before it reaches the outside of the coal particle. Information on the extent of mineral matter activity for catalyzing the carbon-hydrogen reaction to produce methane will also be relevant for the back reaction, which should, in any case, be studied separately.

D. Addition of catalysts to coal

There are particularly large incentives to lower the operating temperature and pressure of the carbon-hydrogen reaction. This is a slow, difficult reaction, which is limited by equilibrium at higher temperatures. Can substances be added to the coal which are very active catalysts for this reaction? Dr. Johnson discusses some possibilities in his section. How important is it that the catalyst be uniformly deposited through the internal porosity of the coal particle? Can the catalyst be recovered following gasification of the coal?

E. Water gas shift reaction

This reaction proceeds concurrently with the steam-carbon reaction. It is important in determining the CO/H_2 ratio in the exit gas. The activity of the minerals in coal for this reaction should also be studied. In some cases, it might be desirable to also study the catalytic activity of added impurities.

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