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STEAM GASIFICATION OF CARBON: CATALYST PROPERTIES

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ABSTRACT

This research uses three techniques to study catalyzed gasification of carbon in an effort to determine the concentration of catalyst sites on a carbon surface and thus determine how effectively a catalyst is utilized for steam gasification. Both alkali and alkaline earth oxides are effective catalysts for accelerating the gasification rate of coal chars, but in many cases only a fraction of the catalyst is in a form that is effective for gasification. We will study the steam gasification of carbon in order to determine the concentration of active catalyst sites, the composition of the catalyst, and the location of the catalyst on the surface. Transient isotope tracing (switching reactant feed gases between H_2^{16}O and H_2^{18}O) will be used to measure the concentration of sites at steady-state reaction conditions. A steady flow of H_2^{16}O in He will be replaced by H_2^{18}O in He, while maintaining the same reaction rate, and the change in product signals will be detected with a computer-controlled mass spectrometer. Secondary ion mass spectrometry (SIMS) will be used for both high surface area samples of carbon/carbonate mixtures that are heated in steam to various temperatures and for model surfaces with deposited ions. SIMS will provide a direct measurement of surface composition. Scanning tunneling microscopy (STM), a technique that provides atomic resolution images of surfaces, will be used to determine catalyst dispersion and the location of catalyst on the surface. The interrelation of the results from these techniques (for potassium and calcium catalysts) will provide knowledge of catalyst dispersion, composition, and utilization. Such knowledge is needed for optimal use of catalysts in steam gasification of coal char.

INTRODUCTION

Coal gasification by steam is of critical importance in converting coal to gaseous products (CO , H_2 , CO_2 , CH_4) that can then be further converted to synthetic natural gas and higher hydrocarbon fuels. Alkali and alkaline earth metals (present as oxides) catalyze coal gasification reactions and cause them to occur at significantly lower temperatures. A more fundamental understanding of the mechanism of the steam gasification reaction and catalyst utilization may well lead to better production techniques, increased gasification rates, greater yields, and less waste.

We are studying the gasification of carbon by steam in the presence of alkali and alkaline earth oxides, using carbonates as the starting materials. Carbon dioxide gasification ($\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$) has been studied in some detail recently, but much less has been done on the actual steam gasification reaction, which is the main thrust of our work. In particular, the form of the active catalyst compound during reaction is still questioned and the dependence of the concentration of active sites on reaction parameters is not known. Until recently, no measurements of active site concentrations during reaction had been made. We have recently used transient isotope tracing to determine active site concentration during CO_2 gasification.

We are investigating the mechanism and the concentration of active sites for steam gasification with transient isotopic tracing. For this technique, the reactant feed is switched from H_2O to isotopically-labeled water at the same concentration and flow rate. We can then directly measure, at reaction conditions, the concentration of active catalytic sites, their kinetic rate constants, and the presence of more than one rate constant. This procedure allows us to obtain transient kinetic data without perturbing the steady-state surface reaction. A mass spectrometer with computer interface allows each of the appropriate mass peaks to be followed in time. The

changes in catalytic site concentrations and their rate constants will be measured as a function of reaction time, initial catalyst concentration, and reaction temperature. Potassium and calcium salts are being used.

The composition of the active catalyst is being studied with secondary ion mass spectrometry (SIMS) for catalyst-carbon mixtures, after high temperature treatment in steam. Model catalyst-carbon surfaces are being prepared so that a planar surface can be obtained for SIMS analysis. Details of the local bonding in reacting solids can also be obtained with SIMS. Scanning tunneling microscopy (STM), a new technique that can obtain atomic images of surfaces with excellent resolution, is being used to determine the location and distribution of catalysts on carbon surfaces. This will be a direct measure of catalyst location and size. By combining SIMS, STM, and transient isotope tracing, we will obtain a detailed understanding of the utilization of the catalyst, its location on the surface, and its chemical form. This information will help in improving catalyst utilization in steam gasification of coal.

OBJECTIVES AND SCOPE OF RESEARCH

The objectives of this research are to determine the catalyst composition and concentration for metal oxide (potassium and calcium oxides) catalyzed gasification of carbon. The scope of this research involves determining:

- The concentration of active catalytic sites (and thus the dispersion), at reaction conditions, as a function of temperature, carbon burnoff, catalyst loading, and catalyst type.
- The location of catalyst, on the surface, on an atomic scale.
- The composition of the catalyst.
- The site-specific rate constant for steam gasification.
- Insight into the reaction mechanism.
- How to maximize catalyst dispersion.

Knowledge of how catalyst dispersion depends on reaction conditions will provide a basis for making optimal use of the catalyst in steam gasification of coal.

RESEARCH PLAN

The catalyst composition, concentration, and location for catalyzed gasification of carbon and coal char by steam will be investigated for both alkali metal and alkaline earth carbonates. Isotope tracing will measure the concentration of active catalyst sites, their specific rate constant, and the dependence of sites on initial catalyst loading, carbon conversion (burnoff), and temperature. Transient isotope tracing, secondary ion mass spectrometry (SIMS), and scanning tunneling microscopy (STM), will be used to obtain a complete picture of the catalysts at reaction conditions.

Carbon black, coal chars, and graphite will be used in the transient tracing experiments. In the SIMS and STM experiments, graphite and carbon deposited on a metal surface will be models of coal char. These forms will allow better utilization of these sensitive surface techniques.

Isotope Tracing Experiments: Transient isotope tracing allows the rate constant and the effective active site concentration to be uncoupled so that a direct measure of reactive site concentration can be obtained. The presence of more than one type of site can also be determined. Isotope tracing can also identify the rate-determining step. We are applying isotope tracing to catalyzed

gasification of carbon by steam. A small amount of carbon, impregnated with K_2CO_3 , will be heated to reaction conditions in a H_2O/He steam. The H_2 , CO , and CO_2 reaction products and unreacted H_2O will be detected with a quadrupole mass spectrometer located immediately downstream from the reactor. Transient mass signals will be measured as $H_2^{18}O$ replaces $H_2^{16}O$ in the feed stream (step increase in $H_2^{18}O$ and step decrease in $H_2^{16}O$). A computer interfaced to the mass spectrometer allows $C^{18}O$, $C^{16}O$, $C^{16}O_2$, $C^{18}O_2$, $C^{16}O^{18}O$, $H_2^{16}O$, $H_2^{18}O$ and H_2 products to be detected simultaneously as a function of time. As soon as the ^{18}O products reach steady state, the $H_2^{18}O$ will be replaced by $H_2^{16}O$ to repeat the process.

Since the partial pressure of steam is unchanged when the isotopes are switched, steady-state reaction is not disturbed, but the isotopic composition of the product mix must adapt itself to the isotopic composition of the feed. A kinetic isotope effect may change the steady-state reaction site, however. This relaxation provides mechanistic information.

These transient isotope experiments will be carried out for a range of reaction conditions to determine what fraction of the catalyst is active for reaction:

- Initial catalyst weight loading will be varied to determine how active site concentration varies with catalyst concentration. The catalyst/carbon ratio will vary with carbon conversion, and thus the concentration of active sites will also be measured as a function of burnoff.
- Reaction temperature will be varied to determine how the number of active sites varies with temperature. At higher temperatures, the loss of K metal can be checked by re-measuring active site concentrations at lower temperatures.
- Both K and Ca catalysts will be used. A better understanding of the role of the catalyst can be obtained by determining the differences between alkali and alkaline earth catalysts.

Secondary Ion Mass Spectrometry (SIMS): Secondary ion mass spectrometry consists of bombarding a surface under UHV conditions with energetic primary ions (typically Ar^+) at sufficient atomic motion to eject particles from the surface. Some of the ejected particles are ionic (secondary ions) and are mass analyzed by a mass spectrometer to give the secondary ion mass spectrum. To prevent significant impact damage to the surface, the experiment is normally conducted in the static mode using a low primary ion current density (typically $1-10 \times 10^{-9} A/cm^2$).

SIMS will be used to probe the identity and reaction chemistry of the species present during catalytic steam gasification. SIMS has unique potential for this since molecular species can be ejected from the surface with their original structure preserved and can therefore be identified directly from the SIMS spectrum.

SIMS will also be used to probe the local chemical environment of surface components. Ejected molecular cluster ions form by reassociation of independently-ejected surface components that are within close proximity of each other (typically 1-5 Å). These molecular clusters are thus indicative of a close proximity between the cluster components on the original surface. This information is essential for a complete understanding of the surface reaction chemistry. SIMS can selectively probe the local environment of such components through the formation of cluster ions containing these components. These capabilities of SIMS for probing the identity, reaction chemistry, and local chemical environment of surface species will be exploited to develop a better understanding of catalytic gasification chemistry.

Carbonate-carbon samples will be examined by SIMS before and after exposure to reaction conditions to identify the chemical species present on the active surface and their local chemical

environment. The effects of reaction temperature, burnoff time, and catalyst loading will be studied for both potassium and calcium catalysts.

Model carbon surfaces will be prepared to produce a cleaner and more well defined carbon surface than that of the carbon black samples, which contain hydrocarbon and oxygenated impurities. Since our previous work shows that the metal-carbonate catalysts thermally decompose to oxides, we will attempt to place the active catalyst on the carbon surface by first vapor depositing, in UHV, the alkali metal and then forming the alkali metal oxide by exposure to oxygen. The nature of the interaction of water with both calcium and potassium oxides on such model surfaces will be determined by SIMS analysis before and during exposure to a H_2O beam in UHV. The effects of temperature, metal oxide coverage, H_2O pressure, and exposure time to the H_2O beam will be studied.

Scanning Tunneling Microscopy (STM): Since the dispersion of the catalyst can significantly affect the reaction rate, we will measure catalyst particle size to determine how dispersion depends on catalyst concentration, surface structure, and temperature. We will also determine the atomic location of the catalyst on the surface. By using graphite with few grain boundaries and thin layers of carbon deposited onto a single crystal metal, we will study the influence of surface structure.

Scanning tunneling microscopy (STM) is nondestructive and yields real-space imaging on an atomic dimension. Experimentally, electric current flows between an atomically sharp needle and the surface of interest. The extreme sensitivity of the tunneling current to tunneling distance is the basis of operation. Tunneling current decreases by roughly ten times for each increase of 0.1 nm spacing. If the needle is scanned laterally across the surface of interest, while the distance between needle and surface is adjusted to maintain a constant tunnel current, the topography of the surface can be obtained. Lateral resolution of 0.1 nm and height corrugations of 0.01 nm have been obtained. The unique advantages of STM are its atomic resolution (individual atoms can be detected) and its direct measure of surface atom location and structure.

PROJECT STATUS, ACCOMPLISHMENTS, AND TECHNICAL DISCUSSION

Most of the effort during this period was devoted to attempts to quantify the number of active sites on the carbon surface. Two types of experiments were used:

1) Treatment in He flow at high temperature to decompose the catalyst precursor, followed by exposure to CO_2/He flow at a lower temperature. The purpose of this experiment is to oxidize the surface species that were reduced at high temperature in He. By using ^{13}C as the substrate and oxidizing with $^{12}\text{CO}_2$, the difference in ^{12}CO and ^{13}CO gives a measure of the number of sites that are oxidized.

2) After steady state $^{12}\text{CO}_2/\text{He}$ flow was attained over the catalyst/ ^{13}C mixture, the feed gas was changed to He (with a Ar tracer to measure the response). The transient response of the ^{12}CO and ^{13}CO provide information on the number of active sites at a given temperature and their rate constant.

Three aspects of these experiments were carried out.

1) Experiments were carried out on carbon samples that contained 6, 10, and 15 wgt % K_2CO_3 . The time necessary to attain steady state CO_2 gasification depended markedly on temperature (conversion). Since efforts were made to keep all conversions low, this is a significant problem. Both overshoot and decay experiments, as described above, were carried out on these samples. The delay problem described below indicates these experiments must be repeated.

2) The Ar tracer indicated that the switching time was 26 seconds and this limited the range of temperatures where experiments could be carried out. It also made analysis of the data difficult. Thus, all the experiments, of the type described above, will be repeated after modifications are completed to the system to solve this problem. An extensive experimental study of the factors that affect the delay time was carried out. Several problems were identified and modifications were made. A filter used to prevent carbon removal from the reactor was replaced with a different type and the delay time was reduced by 12 seconds. The gas injection port was modified to eliminate dead space and the reactor inlet/thermocouple port was redesigned and a new one built in our shop. These two modifications reduced the delay by 10 seconds total. A higher gas flow rate also decreased the delay time by 1-2 seconds. Construction of new parts is complete and the system is now ready for testing.

3) Four methods of data analysis were evaluated for the data obtained to date. Two were concluded to be unsatisfactory because of the complicated mechanism involved. The other two are still being evaluated.

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