LBL-23649
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UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

JUL 31 1987

FUNDAMENTAL STUDIES OF CATALYTIC GASIFICATION:
Quarterly Report, April 1, 1987–June 30, 1987

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July 1987

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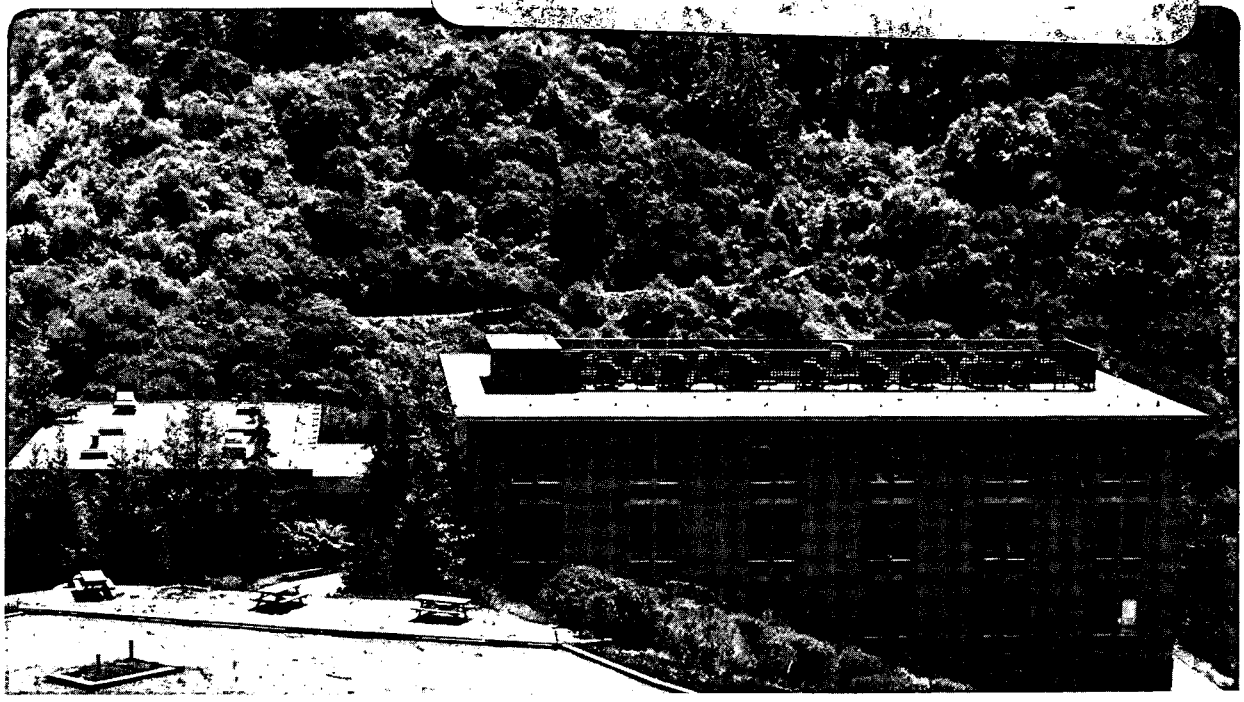

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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QUARTERLY REPORT

April 1, 1987 - June 30, 1987

FUNDAMENTAL STUDIES OF CATALYTIC GASIFICATION

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This work was supported by the Assistant Secretary for Fossil Energy, Office of Technical Coordination, U.S. Department of Energy under Contract DE-AC03-76SF00098, through the Morgantown Energy Technology Center, Morgantown, West Virginia 26505.

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I. Task Description for FY 1987

This program studies the basic chemistry of the reaction of carbonaceous materials with water in the presence of catalysts to produce hydrogen and/or synthesis gas. Relatively low temperatures are being used. The catalysts under investigation are compounds of potassium and a transition metal oxide. Major objectives are the extension of the work from chars to coke; the effect of H_2, CO and CO_2 partial pressure on the gaseous product distribution; and the inhibition of catalyst poisoning by ash components.

II. Highlights

Work during this quarter has been concentrated on the reasons for deactivation of Ni/K catalysts during the steam gasification of chars. Potential interaction of the catalyst with ash components is under investigation as is the possibility that char morphology may change in the course of gasification. Experiments involve flow reactor studies, chemical analyses and surface studies to determine oxidation state and surface concentration of the catalyst.

A large number of data is becoming available but is not presented in this report because it does not yet permit proper correlation and conclusions. It is expected that enough information will be available in time for the next quarterly report to identify causes of and perhaps avenues to circumvent catalyst deactivation.

III. Progress of Studies

During this quarter, the steam gasification of char catalyzed by a Ni/K catalyst has been further studied. The experiments are still in progress, and a complete description of the results will be given in the annual report. In this progress report, a description of the experiments being performed is presented.

The steam gasification of three chars catalyzed by a Ni/K mixture and by Ni and K catalysts deposited alone has been previously discussed. In summary, the Ni/K mixture is more effective for steam gasification of char than for graphite, even though the activation energies and product distribution are similar in both cases. In the case of char gasification, however, the catalyst activity decreases with carbon conversion, and our current experiments are focused toward understanding the reasons for this problem.

Our results indicate that there is a strong interaction between nickel and potassium in the steam gasification of carbon solids leading to a ternary oxide compound formation. Nickel and potassium, however, can potentially also interact with other components present in the char, mainly calcium and alumino-silicate compounds. We have previously reported that the nickel/calcium mixed catalysts are much less active than the nickel/potassium mixture for steam gasification of graphite. The nickel/calcium interaction may therefore be a reason for the loss of catalyst activity. Most of the ash components in the char can be extracted by treatment in aqua regia, and this treatment does prevent the loss of catalyst activity with carbon conversion. The same treatment, however, may also affect the char structure and composition, which in turn can be responsible for the results observed. For example, this treatment strongly oxidizes the carbon surface, and the resulting surface oxygen groups may interact with the catalysts, changing their spreading characteristics and thereby the deactivation process. To distinguish between these two possibilities for catalyst deactivation, that is, interaction with the indigenous components of the char, or change of carbon-catalyst contact, further experiments are being performed. First, pretreatment of the char in HF, instead of aqua regia, can extract the mineral content of the char without oxidizing the carbon surface. Comparison of the results obtained after these two pretreatments can distinguish between these two possible explanations for the catalyst deactivation. Also, based on our surface science results, it is expected that heating of the char at 900 C in vacuum, after the acid extraction

treatment will decompose most of the oxygen surface species, and therefore their importance in the steam gasification process can be evaluated.

Another reason for the catalyst loss of activity could be that the reactivity of the char is not constant with carbon conversion. Certain fractions of the char could be easier to gasify than others due to their porosity, level of graphitization and local concentration of heteroatoms. These fractions would gasify faster, and the catalyst activity would decrease with time. This hypothesis is being tested by reimpregnating with fresh catalyst char samples that have been partially gasified. If the loss of catalyst activity is due to the reactivity of the char, and not to the catalyst poisoning, no significant increase in the gasification activity is expected with the addition of more catalyst.

Parallel experiments in a flow reactor and a surface science apparatus are being performed. The flow reactor studies provide information about the changes in the gasification rates with the various treatments while the surface science studies correlate these changes in rate with oxidation state and surface concentration of the catalyst. With these results a better understanding of the reasons for the deactivation process is expected.

Work is also in progress on gasification of chars with Ni/K catalysts in the presence of external gases such as H_2, CO and CO_2 along with steam. Some difficulties have been encountered in measuring the mixing rates of gases and therewith their partial pressures. Equipment is now being installed to overcome this problem.

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