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Fundamental Studies of Catalytic Gasification

Quarterly Report

October 1–December 31, 1991

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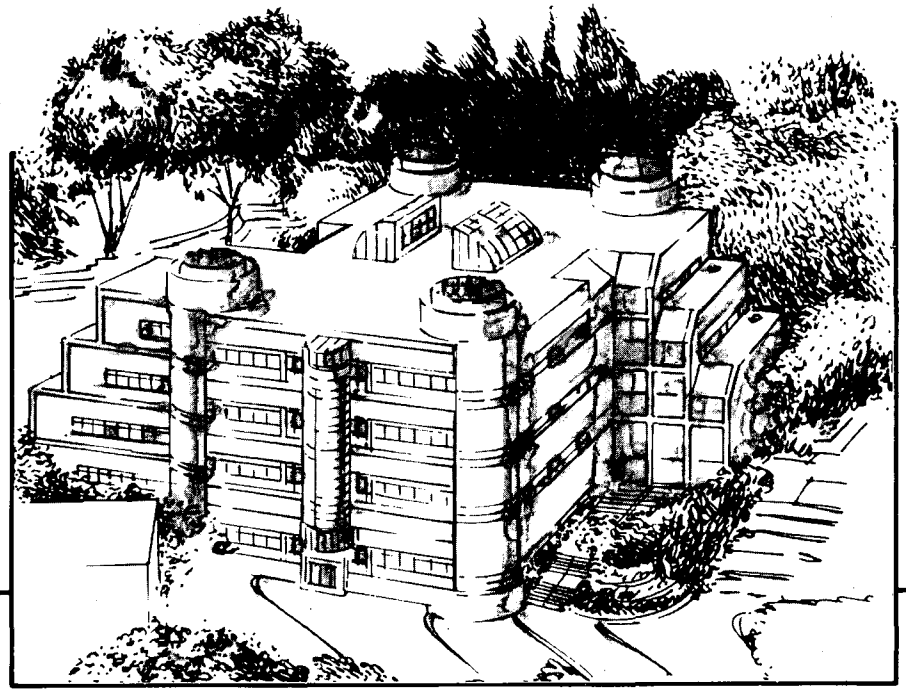

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QUARTERLY REPORT

October 1, 1991 - December 31, 1991

FUNDAMENTAL STUDIES OF CATALYTIC GASIFICATION

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I. Task Description for FY 1992

During the past two years, it has been found that the binary system of good gasification catalysts such as mixtures of potassium and nickel oxide or still better calcium and potassium oxide can be further improved by adding third components to this system. It has also been shown that petroleum cokes can be gasified as easily as coals. Addition of a ternary component such as nickel oxide to the calcium-potassium oxide catalyst has resulted in a material which can oxidatively couple methane to ethane, ethylene, propane, propylene and C_4 hydrocarbons at very high selectivities and at reasonable conversions. The same type of catalyst can also function as a potentially good steam reforming catalyst and may have activity as a hydrocarbon synthesis catalyst for the direct conversion of methane to higher hydrocarbons. The novel nature of this catalyst system needs extensive exploration both of the importance and effectiveness of various components for the ternary system and for an understanding of the mechanisms by which this catalytic system works. The ternary system of oxide catalysts holds the promise of novel reactions for the conversion of carbonaceous material and of low molecular weight hydrocarbons to valuable higher molecular weight hydrocarbons.

II. Introduction

Experimental work during the first quarter of FY'92 was somewhat reduced due to a change of the postdoctoral fellow working on this project.

A potentially important discovery was made in the oxidative coupling of methane, which is the subject of a patent application being drafted and filed and which cannot be disclosed in detail in this report. It is expected that data on it will be included in the next report.

The CRADA between LBL and ACT Orion has been approved by DOE, has been signed, and is now in effect.

III. Highlights

a) Catalytic Steam Gasification of Coals and Cokes

- A gasification unit capable of operating at elevated pressure is being designed and assembled.

- It has been shown that catalytic gasification of petroleum cokes can be greatly accelerated by coking resids in the presence of small amounts of caustic and then impregnating the coke with gasification catalysts. Patent applications are being filed.

b) Oxidative Methane Coupling

- A paper on this subject has been submitted to APPLIED CATALYSIS and a copy is appended to this report.
- The work reported previously on CaNiK oxide catalysts appears to be of a more generic type than expected.

IV. Progress of Studies

a) Catalytic Steam Gasification of Coals and Cokes

A new experimental unit is being built, which will be able to operate at pressures up to 500 psig and over a wide temperature range. With this unit we will be able to extend the work performed during several years from atmospheric to elevated pressure operation. This is, of course, desirable since one would like to produce hydrogen (or syngas) at high pressure.

We have previously shown that petroleum cokes (both from delayed and from fluid bed coking) can be catalytically gasified at the same conditions and about the same rates as subbituminous coals with a CaK oxide catalyst. Metal and sulfur content of the cokes does not seem to influence the rate of gasification. We have now found that when the coking step is carried out in the presence of small amounts of caustic, gasification rates of the coke increase and that if the CaK oxide catalyst is added to this coke, a major improvement in rate is obtained. Patent applications are being prepared and data will be published in a later report.

b) Oxidative Methane Coupling

A paper for publication has been prepared and submitted to APPLIED CATALYSIS which summarizes results obtained with different ranges of variables over the $Ca_3Ni_1K_{0.1}$ oxide catalyst. A preprint of this paper is presented in the appendix.

The major new experimental finding in this quarter has been the discovery of a different catalyst, which when pretreated with oxygen and operated in the presence of steam at the conditions used for the $Ca_3Ni_1K_{0.1}$ oxide catalyst, gives about the same conversions and high selectivity as the earlier described catalyst. No data can be presented until patent applications are filed. However, this finding may indicate that high selectivity coupling with essentially no CO_2 production is generic for a series of catalysts at specific operating conditions.

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