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CATALYTIC GASIFICATION OF GRAPHITE OR CARBON.
Quarterly Report

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QUARTERLY REPORT

April 1, 1986 - May 31, 1986

CATALYTIC GASIFICATION OF GRAPHITE OR CARBON

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I. Introduction

This report only covers the two month period of April and May 1986, since timing in the Principal Investigator's laboratory does not permit a report to be written by the end of the third quarter of fiscal 1986. The final report of fiscal 1986, due on October 1, 1986 will include four months work.

II. Task Description for FY 1986

This program is designed to study the basic chemistry of the reaction of carbonaceous materials with water in the presence of catalysts to produce hydrocarbons and/or synthesis gas. Relatively low temperatures are being used. Earlier work has shown that a combination of KOH and a transition metal oxide, such as NiO, constitutes catalysts superior to either component alone. It is an objective of the present task to identify the optimum ratio of the components and to determine the existence and composition of a potential catalytic compound, e.g. a potassium nickelate. The applicability of the reactions thus far studied with graphite to char, coke and possibly coal will be investigated. Improvements in kinetics will be sought and the effect of added gases, such as H_2S , CO and O_2 will be researched.

III Highlights

1. The previously observed decline with time in the gasification rate of chars impregnated with KOH-NiO catalyst was not observed if the char was treated with aqua regia to remove ash and sulfur ingredients. This indicates that the rate decline is due to a poisoning effect of an ash component, probably sulfur.
2. Controlled Atmosphere Electron Microscopy studies of graphite impregnated with KOH-NiO show a completely different mechanism than nickel or KOH alone. The mixed catalyst wets the edges of the graphite crystals and gasification proceeds by rapid edge recession in contrast to the slower channeling previously demonstrated for the individual components. The low surface tension of the mixed catalyst indicates that it is in the oxide state.

IV Progress of Studies

- (a) Steam gasification of Montana subituminous char after aqua regia treatment.

In the previous quarterly report we presented the rates of steam gasification of five different chars at 893 K catalyzed by a mixture of potassium and nickel oxides. In all cases the initial rate of gasification was one order of magnitude higher than that of graphite. Carbon conversions of up to 50% were obtained after 6 hours. The rates of steam gasification catalyzed by nickel-potassium oxide were in all

cases at least as high as those catalyzed by nickel metal. In the case of Illinois #6 char, the activity of the mixed oxide catalyst was three times higher than that of nickel metal. This higher activity is reflected in a 27% carbon conversion after 6 hours, compared with a 5% conversion in the case of nickel metal and a 6% conversion in the case of KOH catalyst.

The previous results also showed, however, that the nickel-potassium mixed oxide deactivates with time when it is used to catalyze the gasification of char. The deactivation could be due to the interaction between the catalyst and sulfur and/or ash present in the char. Washing the char in aqua regia before reaction is a method widely used to extract minerals, ashes and sulfur from char. The steam gasification results obtained after washing Montana subituminous char in aqua regia are shown in Figure 1. Previously, we reported that on the untreated char, the nickel/potassium oxide catalyst shows an initially high activity that decreases by a factor of three after six hours (Curve A in Figure A). This behavior is very similar to that of the nickel metal catalyst (Curve B). Curve C in Figure 1 shows that when char is washed in aqua regia, the potassium/nickel oxide catalyst retains 90% of its initial activity for steam gasification after a 6 hour reaction period. Even though the initial activity of the Ni/K catalyst for the gasification of the prewashed char is lower than that of the untreated one, after 6 hours its value is 30% higher. Also notice in Figure 1 that the activity of the nickel metal catalyst for the gasification of prewashed char is five times lower than that of the nickel-potassium mixed oxide.

These results support our initial hypothesis that the deactivation of the mixed oxide catalyst is due to poisoning by sulfur and/or ash present in the char. XPS studies of char samples with and without aqua regia treatment and before and after catalyst deactivation will be done to monitor changes in the surface composition and chemical state of the catalyst.

(b) Controlled Atmosphere Electron Microscopy (CAEM) Studies

CAEM studies of the steam gasification of Tindernoga natural graphite, catalyzed by a mixture of potassium-nickel mixed oxide were done in collaboration with Dr. R. T. K. Baker at Exxon Research and Engineering Company.

Qualitatively, the nickel/potassium catalyst presents a completely different mode of attack than nickel metal and potassium hydroxide deposited alone. The nickel-potassium catalyst wets and spreads along all the edges of the graphite surface and attacks the surface by an edge recession mode in the (1120) direction. In previous publications, Evans et al. (1) and Baker et al. (2) have reported that KOH and Ni metal attack the carbon surface by formation of channels. This indicates that in both cases the catalyst only wets the surface and it is not able to spread. In the case of the nickel-potassium oxide catalyst, channel formation is observed above 900°C but in contrast with the case of nickel metal, there was catalyst attack at the walls of the channel by an edge recession mode, causing an expansion of the channel diameter.

An Arrhenius plot of the edge recession rate is given in Figure 2. An activation energy of 31 Kcal/mol was obtained. This value is 4 Kcal/mol higher than the one obtained by us in the flow reactor work.

The different mode of attack of the nickel-potassium catalyst compared with nickel metal and KOH deposited above can be interpreted by the formation of a mixed oxide and agrees with previous surface science studies done in our lab. The excellent spreading property of the catalyst indicates that its surface tension is lower than that of the edge phase of graphite. This is only possible if the catalyst is in the oxide state. Notice that Ni metal and even KOH do not spread on the edge surface of graphite.

The effects of adding H_2 and O_2 to steam in the gasification of graphite catalyzed by a nickel potassium mixture was also studied using CAEM. The results are being analyzed and will be discussed in the next quarterly report.

References

1. Coates, D.J., Evans, J.W., Cabrera, A.L., Somorjai, G.A. and Heinemann, H., J. Catal. 80, 215 (1983).
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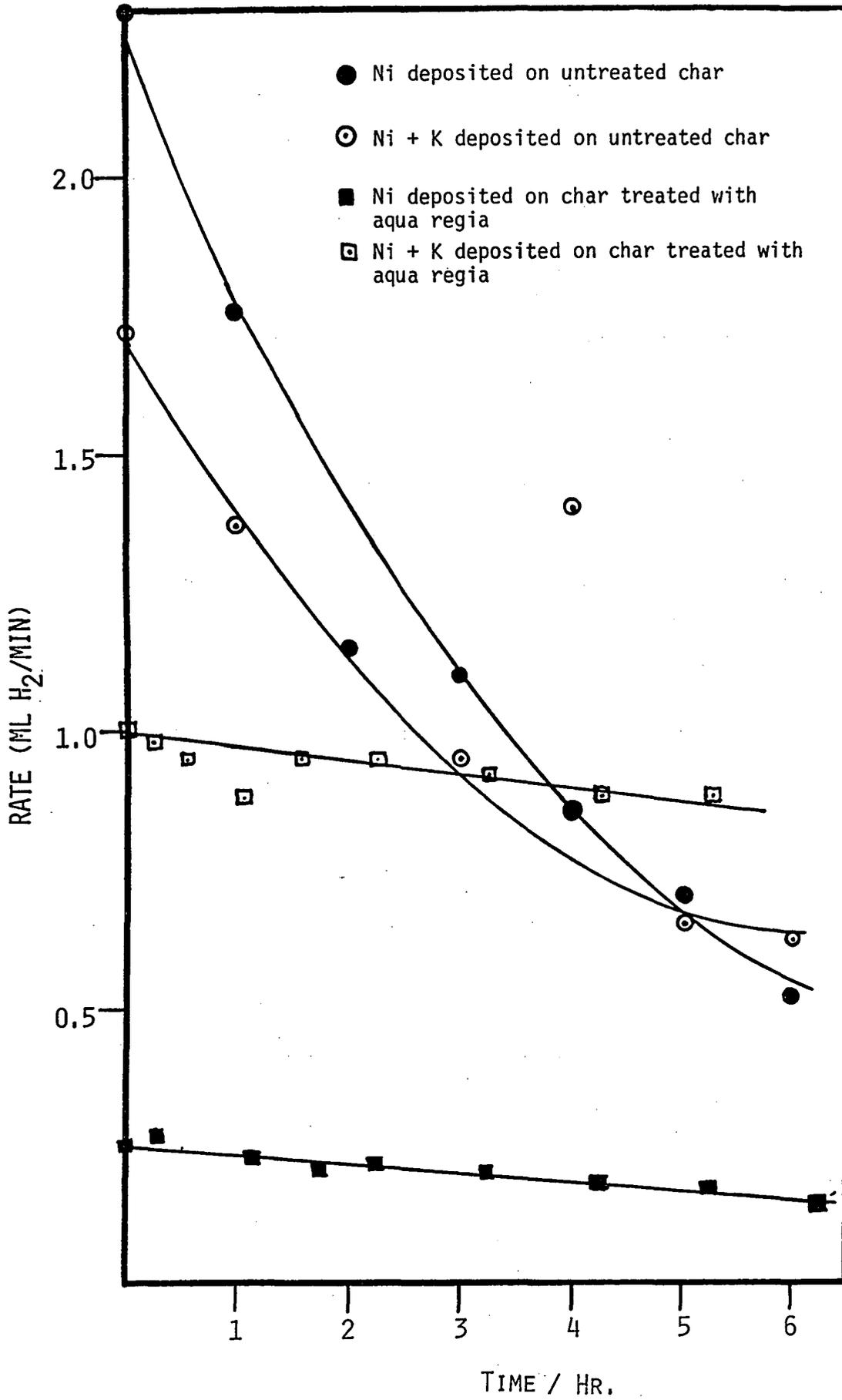
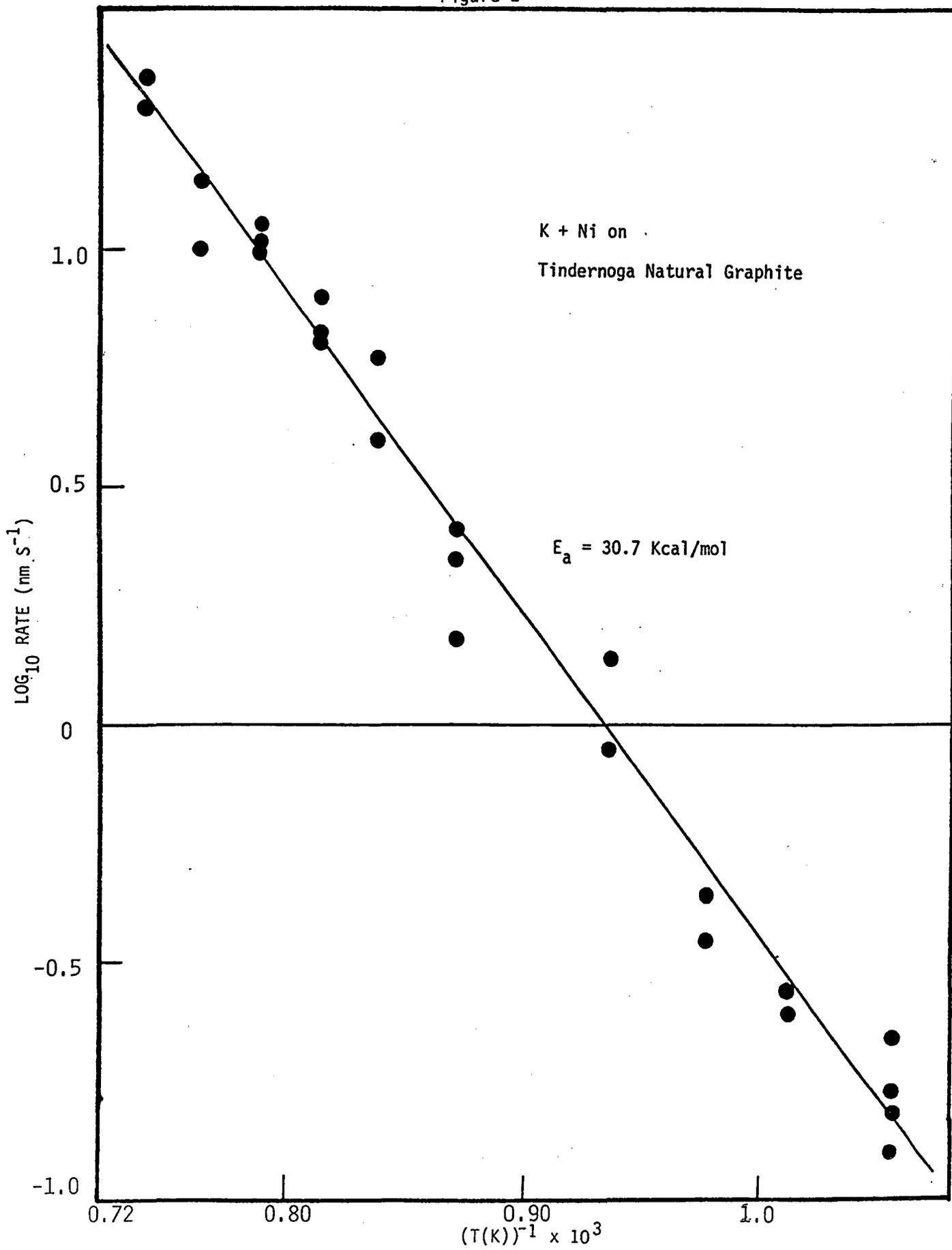


Figure 1

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Figure 2



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