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QUARTERLY REPORT

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FUNDAMENTAL STUDIES OF CATALYTIC GASIFICATION

Principal Investigators: Heinz Heinemann
Gabor A. Somorjai

Center for Advanced Materials
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, CA 94720

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I. Task Description for FY 1990

Our previous work has shown that chars and coal can be gasified with steam in the presence of alkali-transition metal oxide catalysts or alkali-earth alkali catalysts at relatively low temperatures. These studies are to be extended to the investigation of the amounts of catalysts required and whether a throw away catalyst can be used. Fresh versus stored char will be gasified to determine the role of oxidation of the char on gasification rates. Less expensive catalyst materials such as sodium instead of potassium and iron instead of nickel will be explored. Reaction rates will be determined in the presence of nitrogen, CO, and CO_2. Reactions of methane and carbon solids in the presence of an oxidizing agent such as water, oxygen, and/or carbon dioxide will be explored in the presence of similar catalysts. It is expected that hydrocarbon liquids and C_2 plus gases will be produced along with hydrogen. These studies will be performed over a wide range of reaction pressures and reaction temperatures in a flow reactor using a GC-MS detector. Pure paraffinic and cyclic hydrocarbons of high carbon to hydrogen ratio will be gasified to have an indication of the ease of gasification of different carbonaceous materials.

II. Introduction

During the third quarter of the fiscal year, additional experiments on catalytic gasification of coal were carried out. Major emphasis, however, was on the production of C_2 and higher hydrocarbons from methane at very high selectivities.

III. Highlights

a) Coal Gasification

- In the catalytic steam gasification of coals, it has been shown that there is no appreciable difference in rate or time of gasification between a "Premium" freshly mined coal preserved in an inert atmosphere and a coal which has been subject to air oxidation at ambient conditions.

b) Oxidative Coupling of Methane

- The preparation of KCaNiO catalysts for the oxidative coupling of methane with high selectivity to C_2 hydrocarbons is difficile. A large variety of factors in catalyst preparation and reaction operation contribute to catalyst performance.

- Catalysts giving ~100% selectivity at 9-11% conversion can now be produced at will.

- The relative proportion of the catalyst components is of major importance, as is calcination of the catalysts.

- Oxidation pretreatment conditions of the catalyst are critical.

- The best operating conditions are temperatures of $560\text{-}600^{\circ}C$ and low space velocity at atmospheric pressure.

- The presence of steam is essential for selectivities approaching 100% as well as for stable operation over extended periods of time.

- The mechanism of the coupling of methane in the presence of oxygen and of steam over KCaNi catalysts appears to be different from the mechanisms proposed in the literature for coupling at higher temperatures and with lower selectivities. A homogeneous gas phase mechanism does not appear to exist in the present work and a reaction on the surface appears to be predominant.

IV. Progress of Studies

a) Coal Gasification

Coal samples previously used in this work had been obtained from IGT and had been stored there and in our laboratory under conditions which may have led to a surface oxidation of the coal. We have now obtained from the coal bank at Argonne National Laboratory samples of "Premium" coals which were mined, crushed and stored under atmosphere controlled conditions and which can be assumed not to have been contaminated by atmospheric oxygen. The Pitt #8 Franklin "Premium" coal has been gasified under our standard conditions and compared with the gasification of the same coal which had been stored without precautions. Figure 1 presents a rate vs conversion plot for the "Premium" coal in the absence of catalyst and for both coals in the presence of $KCaO_x$ catalyst. Figure 2 shows the same data as a conversion vs time plot. The "Premium" coal in the absence of catalyst showed only very minor gasification characteristics at standard conditions. The two coal samples impregnated with 1% $KCaO_x$ behaved very similarly with a slight advantage for the air exposed coal. It is concluded that exposure to air is not detrimental to the gasification of coals and that no special precautions have to be taken in preparing the coals for gasification.

b) Oxidative Coupling of Methane

In our quarterly report of March 31 (LBL-28710, UC-113) we described the performance of a KCaNiO catalyst which gave selectivities to C_2 hydrocarbons of 100% at conversions of about 10%. Since then we have encountered severe problems in reproducing other samples of this catalyst. We have spent about two months learning how to prepare active and stable catalysts and can now produce them at will. This has involved careful bulk and surface analysis of the catalysts as well as reaction studies. Patent applications are being filed on the catalyst preparation and operation and detailed information must therefore be withheld at this time.

Factors of importance in the catalyst preparation are: The proportioning of the components; the sequencing of the components; the calcination and oxidation conditions of the catalyst.

Important factors in operation are: temperature; space velocity; presence of steam.

Under the best combination of variables thus far obtained, a stable selectivity of 96-98% selectivity to C_2 was observed at ~9% conversion of CH_4 as shown in Fig. 3. This corresponds to a selectivity of 100% because in a blank run without catalyst about 3% conversion to CO_2 was observed. It is concluded that some homogeneous gas phase reaction occurs in the absence of catalyst in the preheat zone of the reactor and results in selectivity to CO_x of 2-4%. There was no catalyst deactivation over 6 hours of operation (ratio A of Fig. 3). With a slightly different catalyst composition, the selectivity was 79% and showed a greater decline as a function of time (ratio B in Fig. 3).

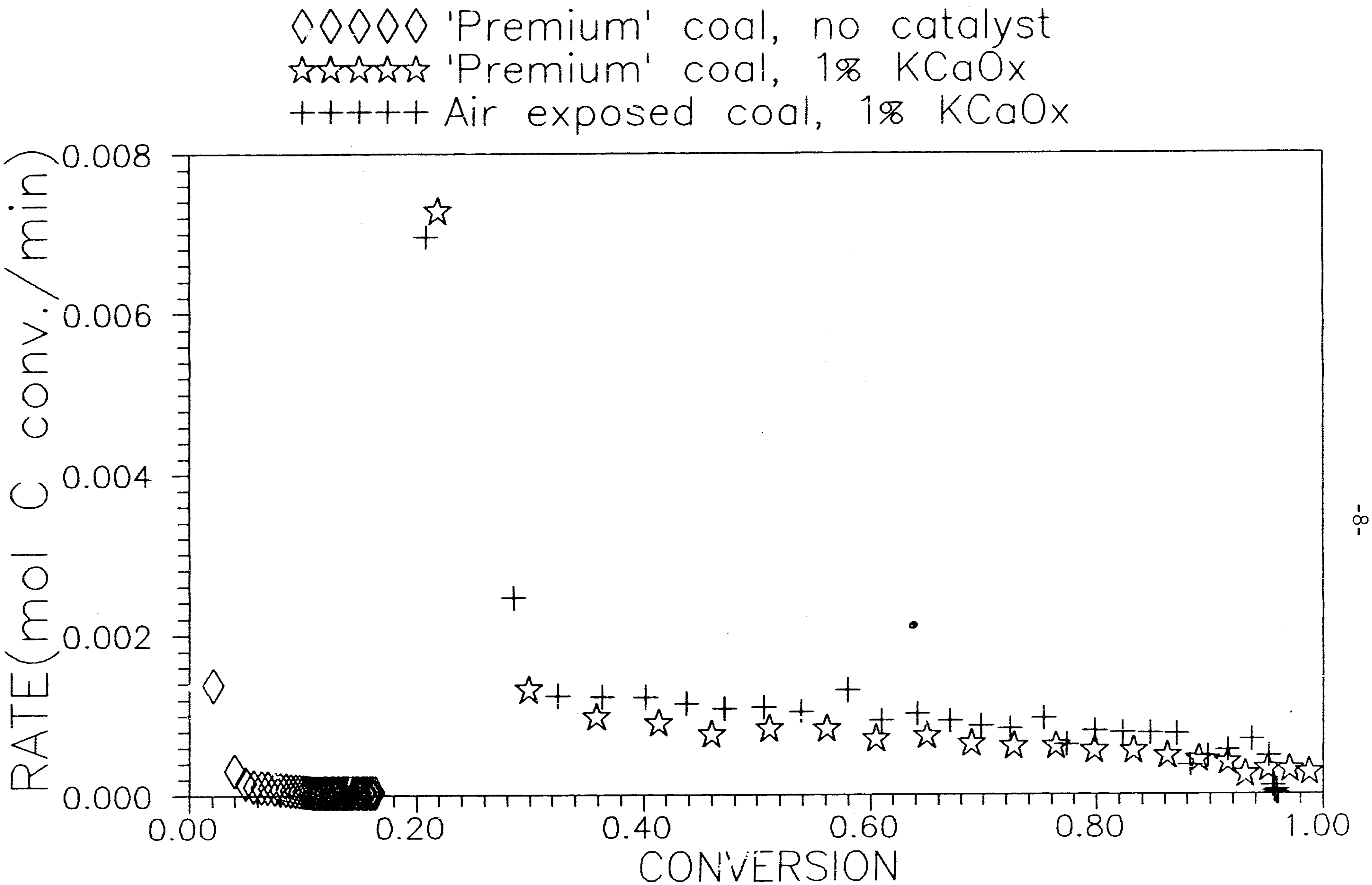
Figure 4 demonstrates that for other compositions and pretreatments of the KCaNi catalyst wide variations of C_2 yields are obtained, all at less than 100% selectivity, indicating the importance of proper catalyst preparation.

Material balances for carbon were checked for a number of catalysts. Figure 5 shows that after an initial induction period the carbon weight balance was 100%. The induction period is observed with all catalysts of the KCaNi type tested at a variety of conditions. It is believed that the mechanism of the oxidative coupling of methane over these catalysts and at these conditions is different from that proposed in the literature and does not involve a homogeneous gas phase reaction, but consists of a catalytic surface reaction. It seems likely that methane decomposition is an initial step, laying down an active carbon species on the catalyst surface, which is thus modified. This would explain a lower than 1:1 carbon balance between feed and production in the initial stages of operation.

The importance of operating at relatively low temperature (560-600^{o}C) has been shown in the last quarterly report (LBL-28710, UC-113, Fig. 1 and Fig. 2). This has since been confirmed. Figure 6 presents an evaluation of the importance of the presence of steam in the reaction. When steam was replaced with helium (same partial pressure of CH_4 and O_2) the selectivity to C_2 hydrocarbons at 600^{o}C dropped from 95 to 87% and rapidly declined further to 25%. Steam was then reintroduced at 700^{o}C and the selectivity recovered to 65%, only to drop rapidly to 35%. Raising the temperature further to 750^{o} again gave a temporary increase in selectivity to 48%. When the temperature was lowered to 600^{o}C in the continued presence of steam, the selectivity returned to over 90% and appeared stable. The yield of C_2 hydrocarbons (product of conversion and selectivity) was fairly steady at 8-12% during operation with steam, but dropped to 1-2% during operation with helium (Fig. 6).. It is concluded that the presence of steam is essential for the reaction and that low temperature is important for high selectivity.

The importance of pretreatment of the finished catalyst with oxygen is illustrated in Table 1. It shows the conversion and selectivity to various hydrocarbons of the same batch of catalyst after pretreatment in flowing oxygen at reaction temperature for different periods of time. It is obvious that long time oxidation is required. Catalysts thus prepared give higher conversion and are then stable over long periods. It is also important that production of some C_3 hydrocarbons occurs in addition to C_2 hydrocarbons. In all cases presented in this table the conversion to CO_2 was the same (3-4%) and was identical with that obtained in a blank run in the absence of catalyst. It has, therefore, been omitted from the table and total hydrocarbon selectivity has been stated at 100%.

No attempt has yet been made to increase conversion at 100% selectivity, though a number of possibilities suggest themselves and no attempt has yet been made to change olefin/paraffin ratios.



STEAM GASIFICATION OF PITT. #8 FRANKLIN COAL AT 640 C,
0.5 g. of sample, water flow:4 g./h.
'Premium' coal is compared to a long time air exposed
coal in presence or absence of KCaOx catalyst.

Fig. 1

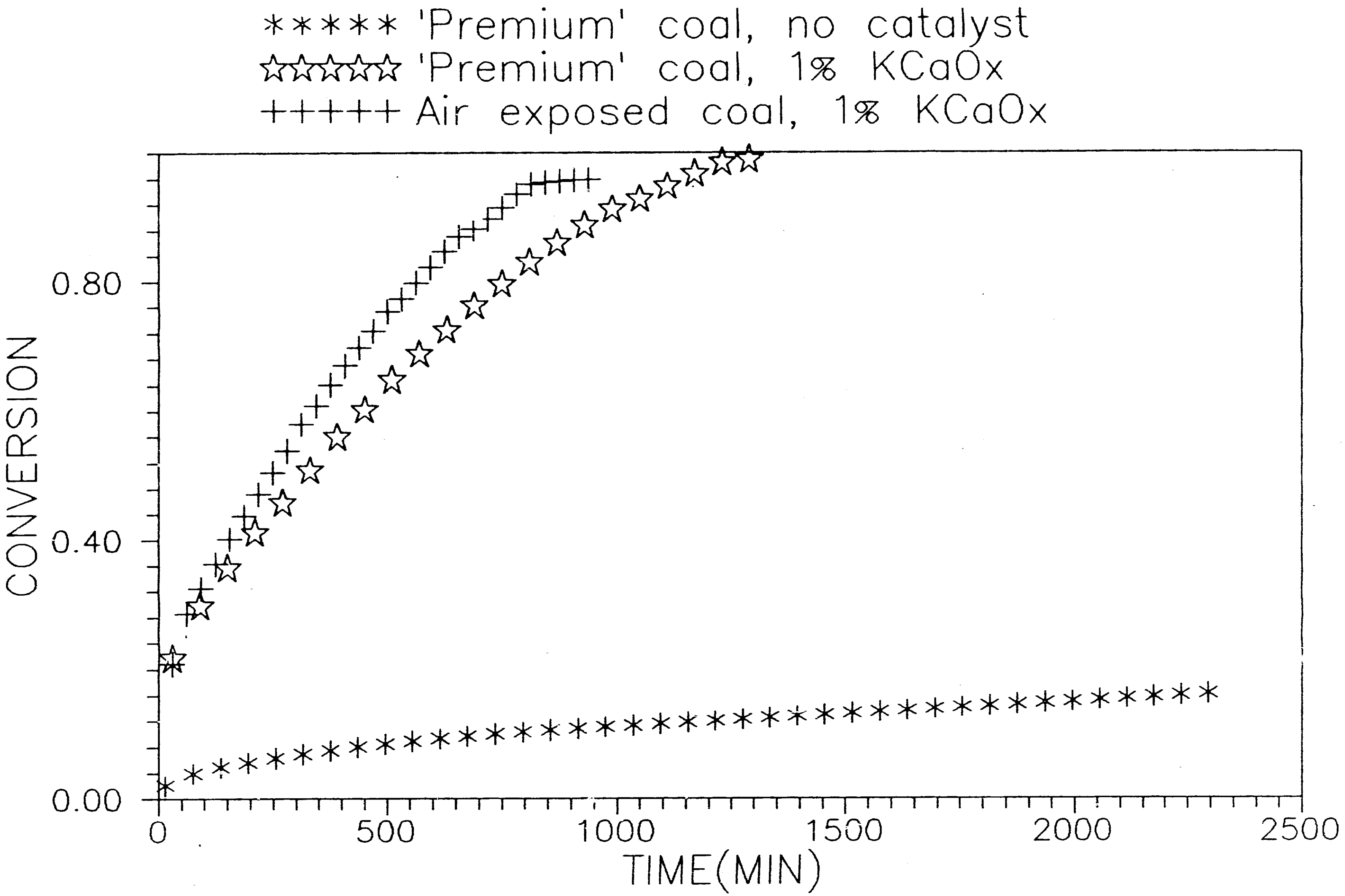


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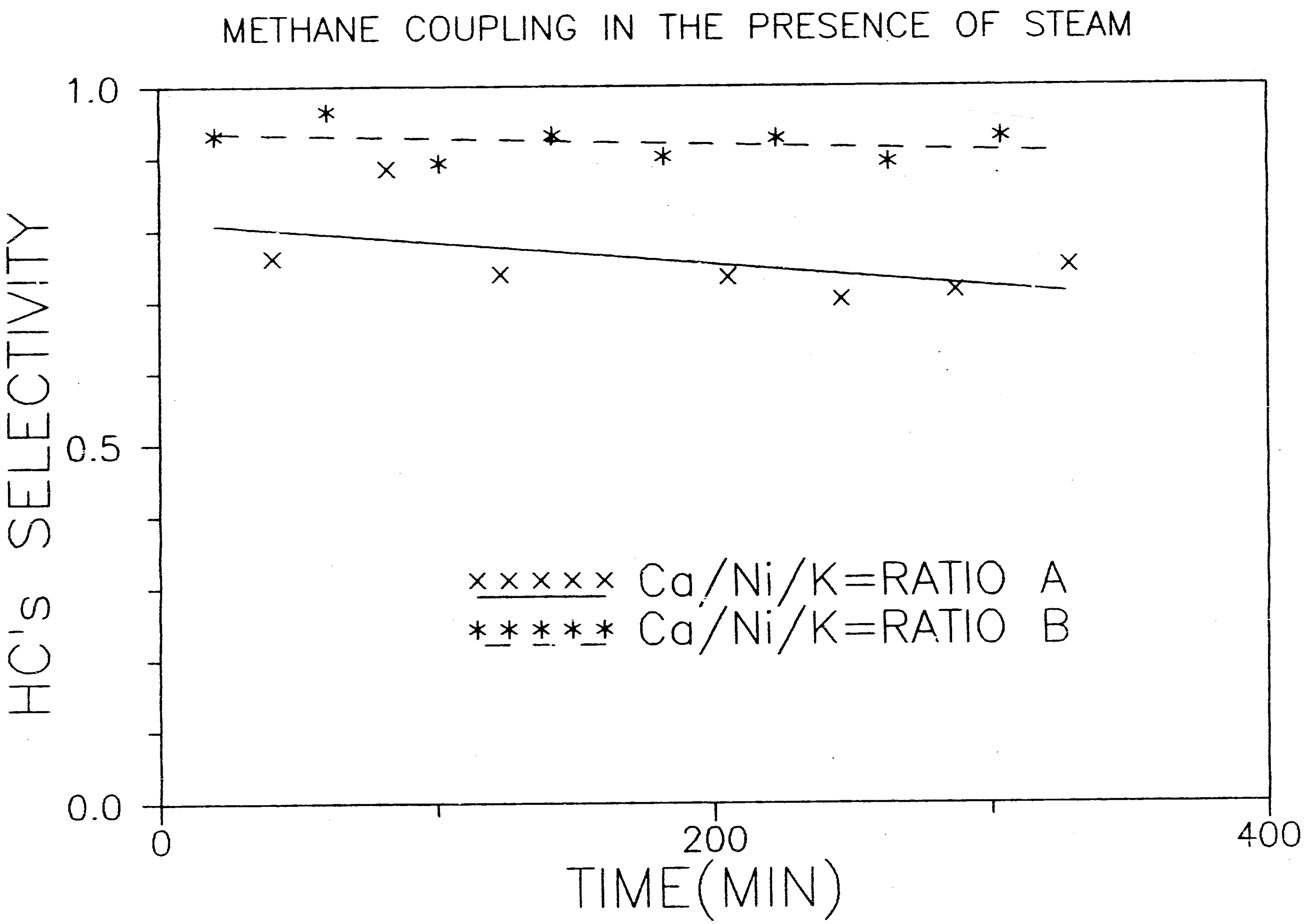
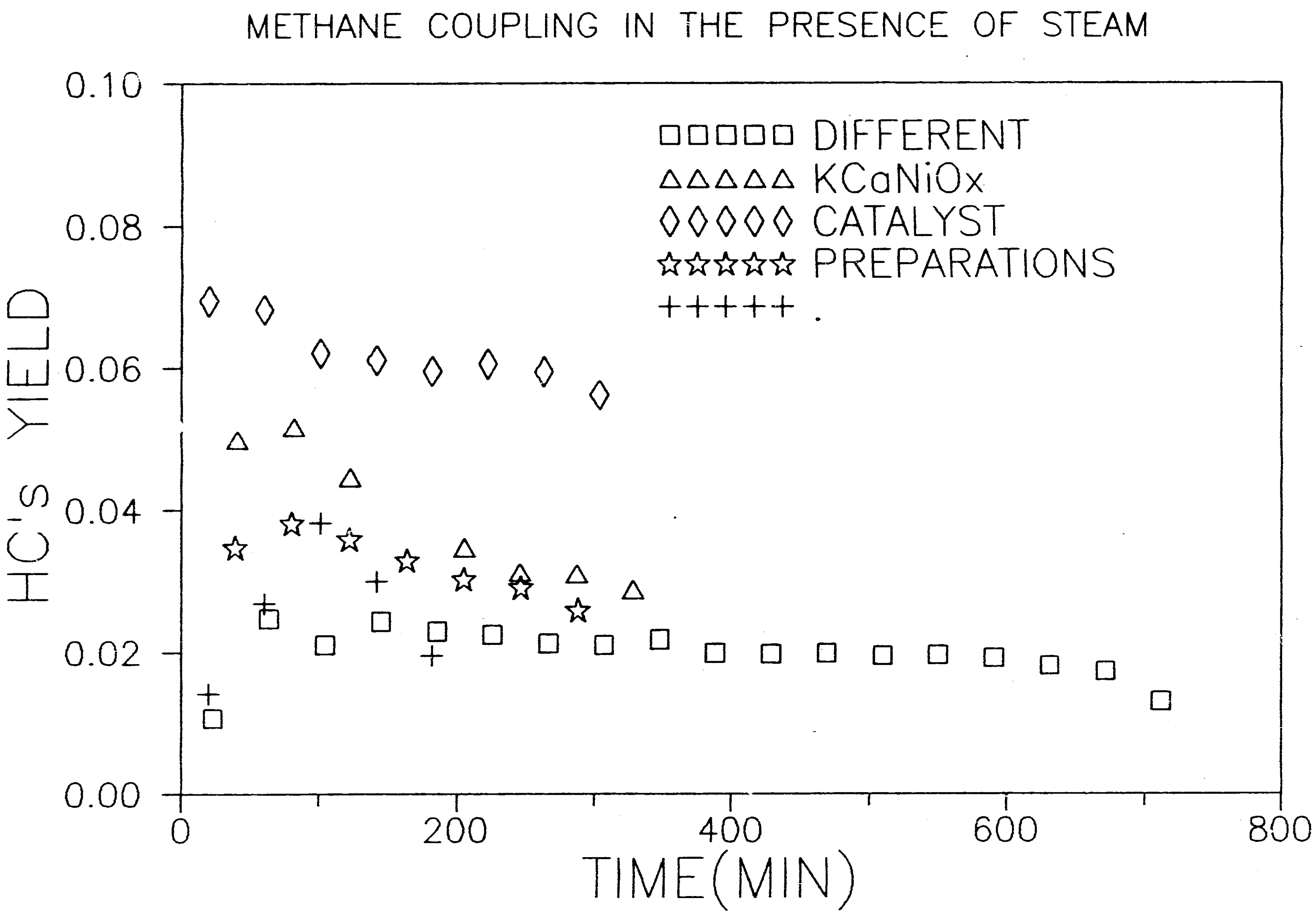
Fig. 2



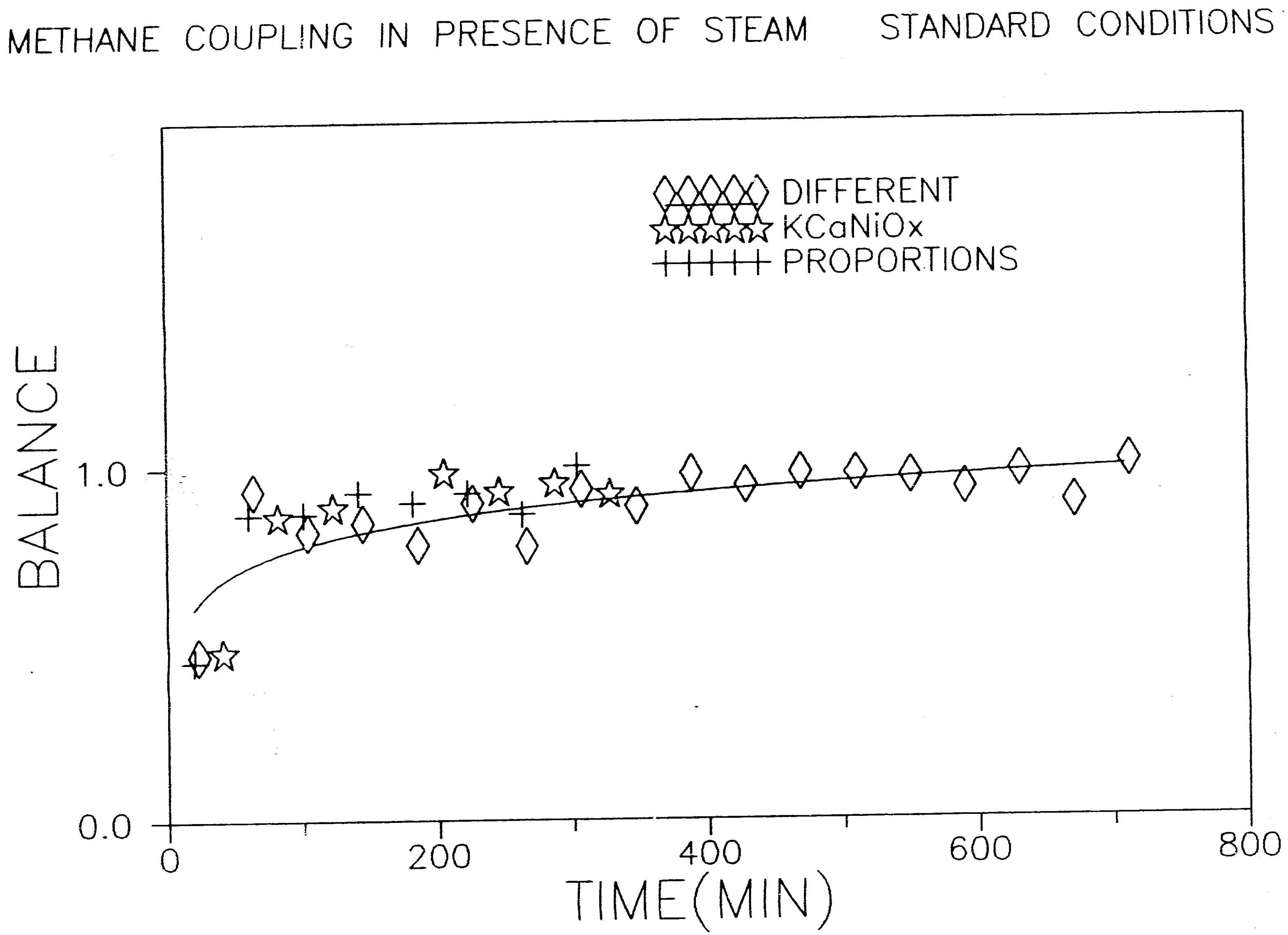
EFFECT OF COMPOSITION ON THE SELECTIVITY TO HYDROCARBONS
STANDARD CONDITIONS

Fig. 3



EFFECT OF COMPOSITION ON THE SELECTIVITY TO HYDORCARBONS
STANDARD CONDITIONS

Fig. 4



MATERIAL BALANCE FOR CARBON. PERFORMANCE vs. TIME FOR THE MOST SELECTIVE CATALYSTS.

Fig. 5

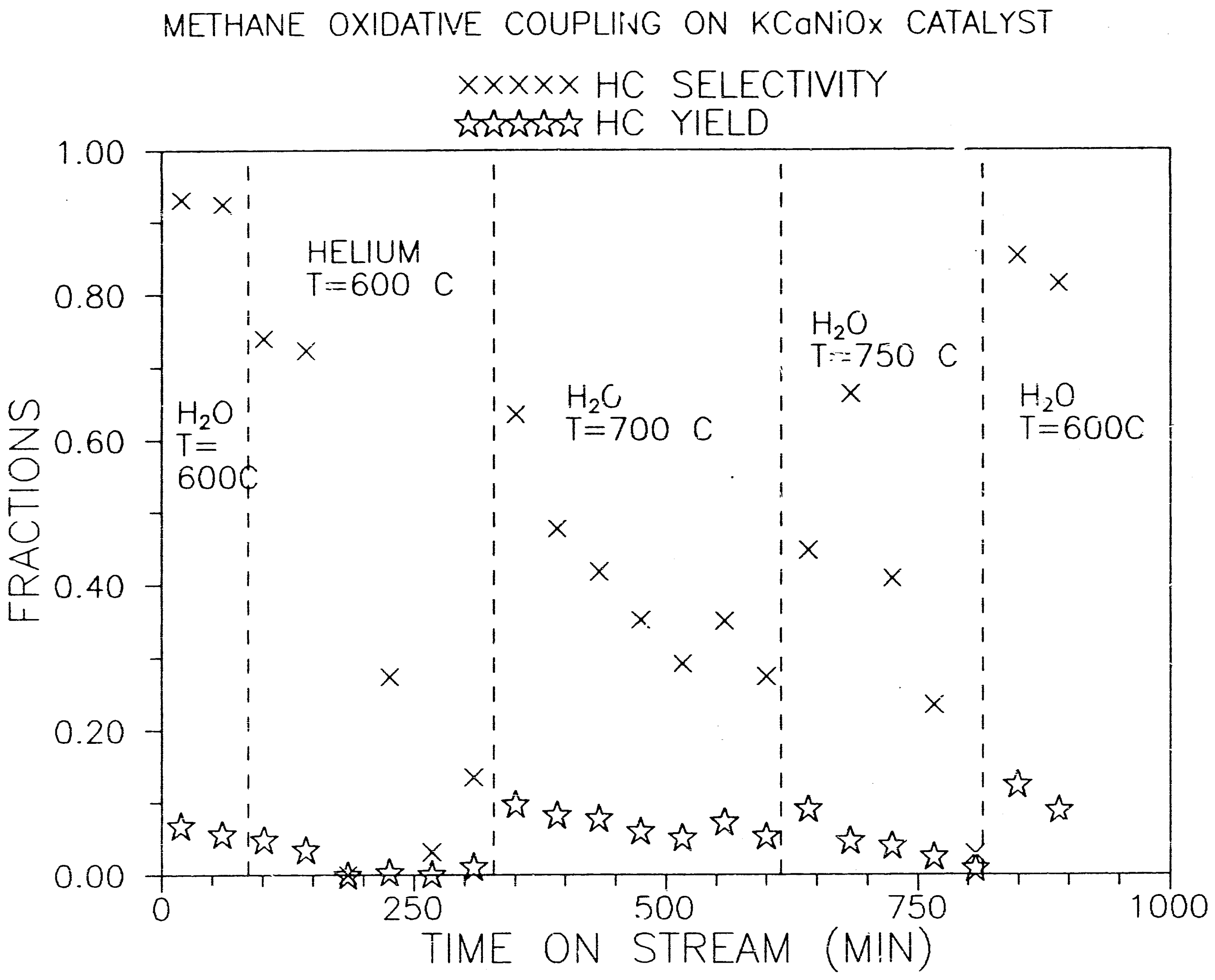

METHANE OXIDATIVE COUPLING ON KCaNiOx CATALYST
××××× HC SELECTIVITY
☆☆☆☆☆ HC YIELD
FRACTIONS
1.00
0.80
0.60
0.40
0.20
0.00
0
250
500
750
1000
TIME ON STREAM (MIN)
H_2O T= 600C
HELIUM T=600 C
H_2O T=700 C
H_2O T=750 C
H_2O T=600C

Fig. 6

TABLE 1

Effect of the in-situ activation of the catalyst.
Activation was with oxygen prior to reaction.

Activation time (Hours) (O_2 2ml/min)	% Conversion of CH_4	% Hydrocarbon Selectivity	% $C_2^=$ Selectivity	% C_2^- Selectivity	% $C_3^=$ Selectivity	% C_3^- Selectivity	% C_4^+ Selectivity	Total Olef/ Paraf.
1	1.8	100	16.0	82.0	0	2.0	0	0.19
18	6.6	100	32.3	57.1	2.7	5.8	2.1	0.56
40	9.5	100	38.1	48.2	5.3	5.6	2.8	0.81

Selectivity was assumed 100% because CO_2 production was always below the blank run values and approximately constant.

END

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