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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

This report covers work performed during the first quarter of fiscal 1990. The period was marked by some experimental difficulties which have now been largely cleared up. A paper on more recent work was written and has been accepted for publication in THE JOURNAL OF CATALYSIS. This paper is appended as Appendix A of this report.

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Earlier work had indicated that the type of catalyst used in the steam gasification could also perform in the oxidative coupling of methane to C_2 hydrocarbons. It appeared that the presence of carbon and water was important in this reaction which showed thermodynamic feasibility. This phenomenon was further investigated and early results are described in the second part of the present report.

III. Highlights

A) Carbon Gasification

- The effect of methanol as a solvent in catalyst impregnation has been evaluated. It was found to decrease the gasification rate for the steam carbon reaction. This is probably a result of a non-edge selective dispersion of the catalyst particles.

- A third metal component was introduced into the $KCaO_x$ catalyst in an attempt to enhance carbon-carbon bond breakage. Using Ni as the third component, poorer results were obtained than with $KCaO_x$ alone.

- Substitution of other alkali and/or earth alkali oxides for K and Ca showed that sodium is equivalent to potassium,. A cesium-barium oxide catalyst is comparable to $KCaO_x$ in overall performance. It is less active initially, but more active in the later stages of gasification.

- The superiority of $KCaO_x$ over $KNiO_x$ for char gasification has also been demonstrated for the gasification of the parent coals.

B) Methane Coupling

- Thermodynamic calculations show the feasibility of relatively low temperature production of C_2 hydrocarbons from methane, oxygen, water, and carbon.

- Yields of C_2 hydrocarbons of about 13% at 16% CH_4 conversion and 80% selectivity to C_2 were obtained at 640°C using $KCaO_x$ catalyst derived form char gasification and in the presence of water. This is at about 150°C lower temperature than equivalent yields with alkali-earth alkali catalysts reported in the literature.

- The presence of carbon in the preparation of the catalyst appears essential, since much poorer results were obtained with unsupported or silica or alumina supported $KCaO_x$ catalysts.

- The initial $KCaO_x$ to carbon ratio appears to be important, with low ratios giving better results.

- Only very small amounts of catalyst were present in the flow reactor after gasification of the carbon, suggesting bypassing and lower conversion of CH_4.

- In addition to carbon, the presence of water is important. Yields of C_2 hydrocarbons are lower in the absence of water, even if partial pressures of other feed materials (CH_4, O_2) are kept constant.

IV. Progress of Studies

A) Steam Gasification of Chars and Coals

Catalyst dispersion on the surface and in the pores of the carbonaceous material can be expected to be of importance during gasification. In a first approach, a catalyst solvent for impregnation other than water was investigated to observe different wetting effects. A solution of 20% methanol in water was used to impregnate Kentucky #13 char with K-Ca oxide catalyst. It was expected that methanol would reduce the hydrophobic nature of carbon for water. The results shown in Fig. 1 indicate that poorer gasification occurred when using the methanol-water solvent than with pure water. This may be due to water as solvent depositing catalyst predominantly on carbon crystal edges, while the methanol containing solvent gives a more evenly distributed deposition. It has previously been shown that gasification occurs by edge recession. If this hypothesis is correct, one might deduce that differences in activity observed for different coals and chars maybe due to differences in edge density rather than penetrability.

Another negative result was obtained when it was attempted to improve the K-CaO_x catalyst by incorporating a third oxide component. A standard $KCaO_x$ impregnated Rosebud coal was further impregnated with $Ni(NO_3)_2$ solution (Ni=1/2 of molar K-Ca content) and then dried and decomposed by standard procedure. Fig. 2 shows that the thus prepared coal was less active than the K-CaO_x impregnated coal, perhaps because the Ni blocked access to some of the $KCaO_x$ sites.

Figure 3 extends earlier work (LBL report 27805) comparing the relative activity of $KNiO_x$ and $KCaO_x$ catalysts from chars to coals. Ohio Franklin Pitt #8 coal was impregnated with $KCaO_x$ and with $KNiO_x$. Just as in the case of chars, $KCaO_x$ was more active in gasifying the coal than was $KNiO_x$. This result further confirms earlier conclusions that $KCaO_x$ is more active than $KNiO_x$ for high rank coals.

Impregnation of Franklin Pitt #8 coal with other alkali and/or earth alkali oxides was undertaken. It had previously been shown that Na could be substituted for K without adverse effects. Using a cesium-barium nitrate aqueous solution for impregnation and following the standard drying and decomposition procedure, the $CsBaO_x$ catalyst behaves similarly to $KCaO_x$. Figure 4 shows $CsBaO_x$ performance characteristics and Fig. 5 compares $CsBaO_x$ with $KCaO_x$. The main difference is that $KCaO_x$ exhibits a higher activity during the first half of the gasification, but a somewhat lower activity during the second half. $CsBaO_x$, therefore, demonstrates a more level performance throughout the gasification. This difference maybe attributable to the bigger ionic size of Cs and Ba and their dispersion on the coal particles.

B) Oxidative Coupling of Methane

Figure 6 presents thermodynamic calculations of the feasibility of a $C+CH_4+H_2O+O_2$ reaction to $C_2H_4+CO_2+H_2+H_2O$.

When methane and oxygen in a 6:1 molar ratio were introduced into the $KCaO_x$ catalysed steam gasification of a Kentucky #13 char at 685^oC no methane coupling was observed until about 95% of the char had been gasified (LBL-27330). Figure 7 shows that C_2H_4 and C_2H_6 then rapidly increased and leveled off at about 40% selectivity for C_2 hydrocarbon each at 16% CH_4 conversion for a total C_2 yield of about 13%. Much the same results were obtained for $KCaO_x$ on Rosebud char (Fig. 8). It is important to note that 80% selectivity to C_2 at 15-20% conversion is obtained at temperatures about $100-150^oC$ lower than those reported in the literature for similar results on unsupported alkali-earth alkali catalysts.

The initial KCa/C ratio was investigated for its effect on methane coupling after essentially complete gasification of the Rosebud char. Table 1 shows that the lowest ratio (0.01% catalyst on char) gave the best coupling yield and that the C_2 yield (product of conversion and selectivity) decreased as the percent of catalyst on char increased.

It must be emphasized that all the data presented here were obtained in a flow reactor which originally contained 1-2 gram of impregnated char. Since almost all the carbon in the char was gasified when C_2 hydrocarbon production started, extremely small amounts of active catalyst were then present and bypassing of feed must have occurred, reducing the amount of CH_4 conversion observed.

A pellet of unsupported $KCaO_x$ was prepared as were pellets of $KCaO_x$ on silica. As shown in Fig. 9 the C_2 yield obtained with the catalyst derived after char gasification was appreciably higher than that observed with the unsupported catalyst and much higher than that with the catalyst supported on SiO_2. This seems to indicate the importance of carbon, either as an initial support or as a participant in the reaction. The unsupported pellet catalyst required a substantial induction period before it reached steady state performance.

The importance of the presence of water for the coupling reaction was studied at 640°C. In this case a relatively inactive $KCaO_x$ catalyst derived from impregnation on alumina wool was used, since large enough quantities of catalyst derived from char gasification were not available. Fig. 10 shows that there was little difference in CH_4 conversion (8-9%), but a major difference in C_2 selectivity. A selectivity of about 50% was obtained in the presence of steam while the selectivity to C_2 was only about 23% in the absence of steam. This illustrates the need for the presence of water in the reaction. Increasing the temperature from 640 to 680°C in the presence of steam lowered both conversion and selectivity over this catalyst. It should be noted that both conversion and selectivity were constant over extended periods of time.

Using the relatively low activity $KCaO_x$ catalyst on SiO_2, the effect of water flow and of temperature was investigated. FIg. 11 shows that selectivity to C_2 is highest at a higher water flow and low temperature, but that conversion increases with lower water flow and higher temperature. The best C_2 yield was obtained at intermediate water flow and intermediate temperature. It is not clear from this whether the effect of water on yield is due to participation of water in the reaction or to changes in the various partial pressures of reactants due to changes in water partial pressure. Fig. 12 indicates that the C_2 yield over this catalyst increases with water partial pressure up to about 80% partial pressure when total pressure was kept constant with use of a helium stream. This infers that water is a participant in the reaction rather than a diluent.

TABLE 1.

Oxidative methane coupling in presence of water with $KCaO_x$ catalyst derived from steam gasification of Rosebud char.

WHSV = 270 H^{-1}; Temp: 681-4°C; P = 1 atm

Initial KCa/C	C_2 Yield @ 60h time on stream
0.01	11.9
0.05	10.1
0.10	9.1
0.53	6.0

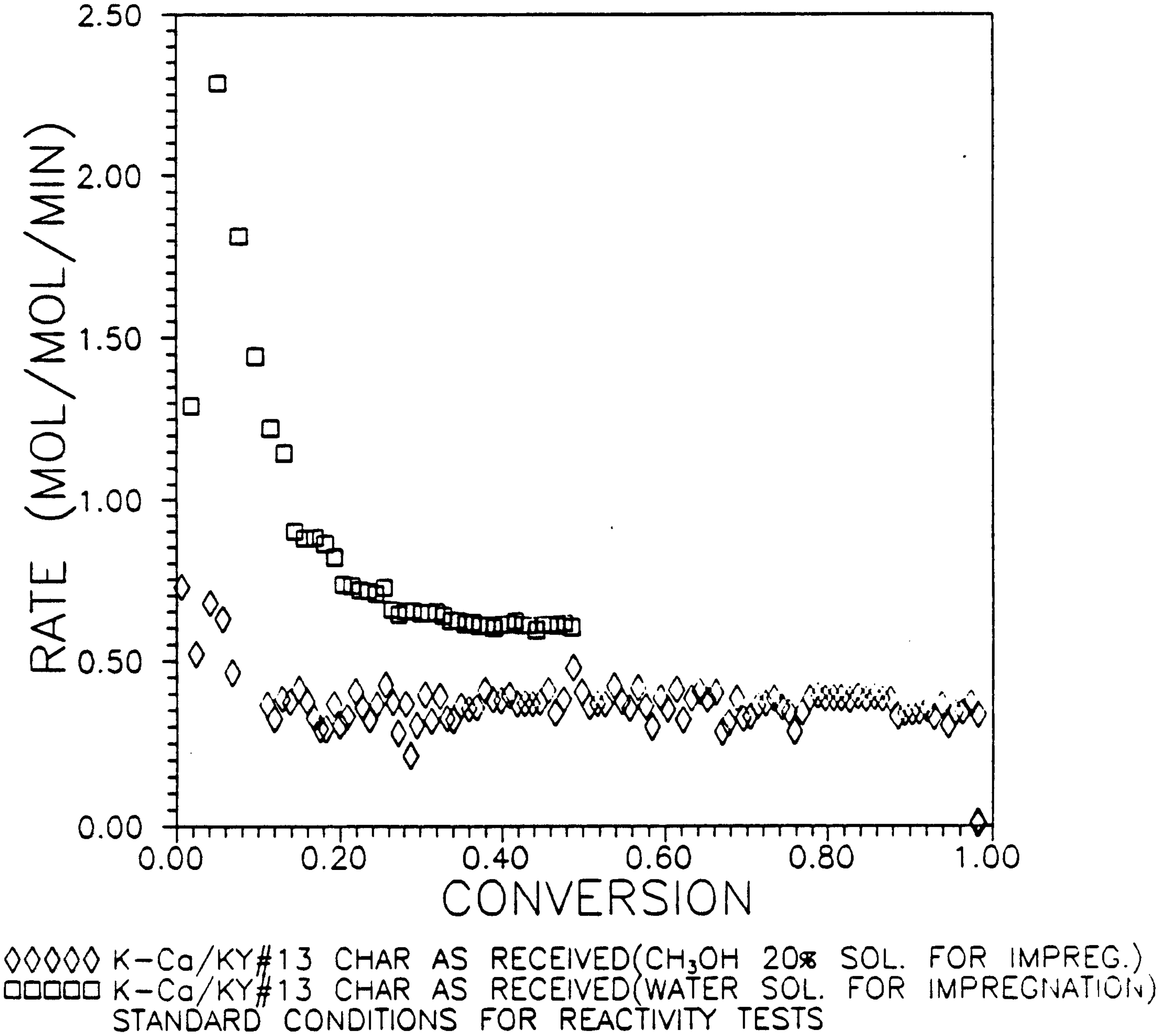

2.50
2.00
1.50
1.00
0.50
0.00
RATE (MOL/MOL/MIN)
0.00
0.20
0.40
0.60
0.80
1.00
CONVERSION
◊◊◊◊◊ K-Ca/KY#13 CHAR AS RECEIVED(CH₃OH 20% SOL. FOR IMPREG.)
□□□□□ K-Ca/KY#13 CHAR AS RECEIVED(WATER SOL. FOR IMPREGNATION)
STANDARD CONDITIONS FOR REACTIVITY TESTS

Fig. 1

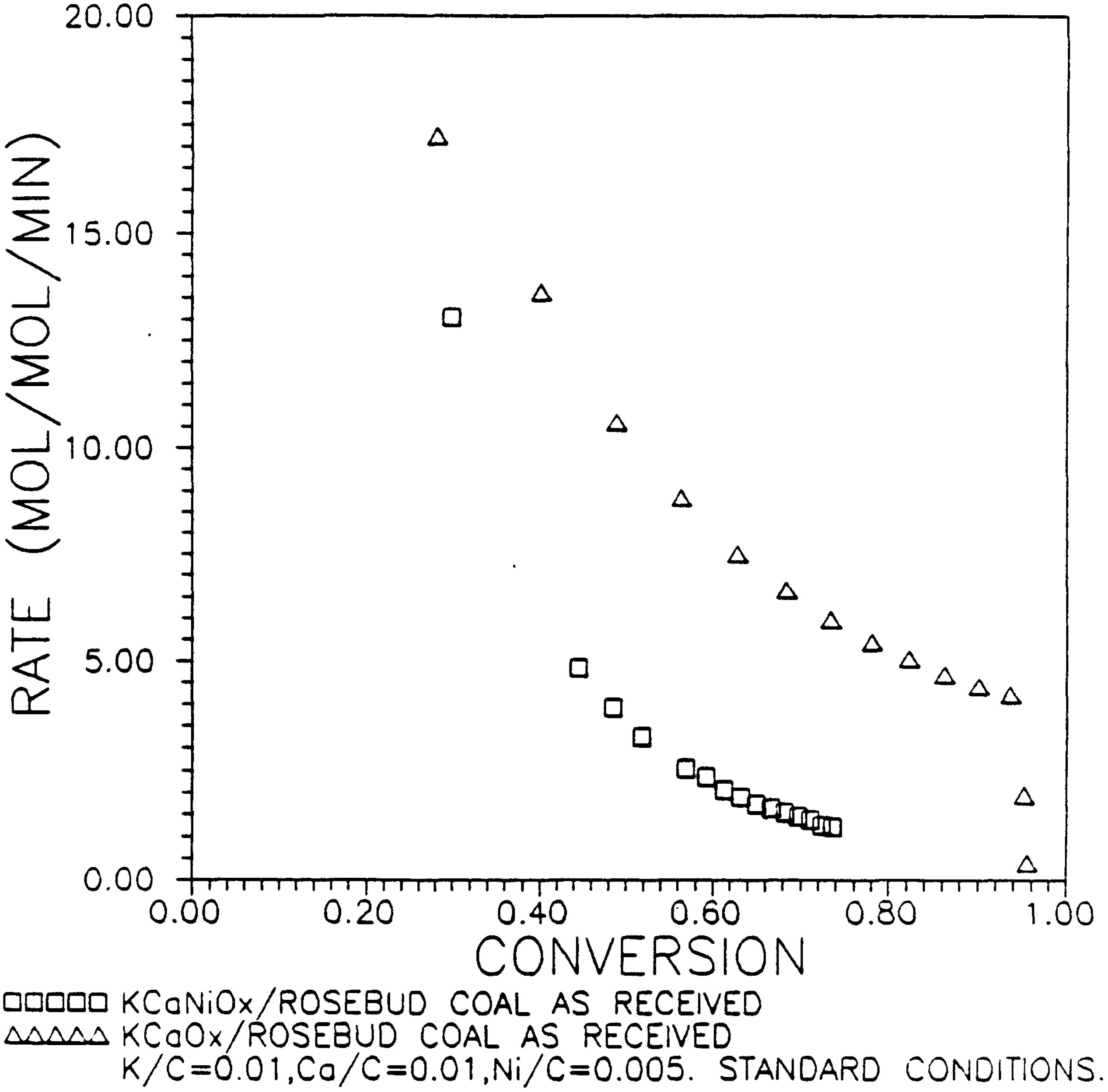
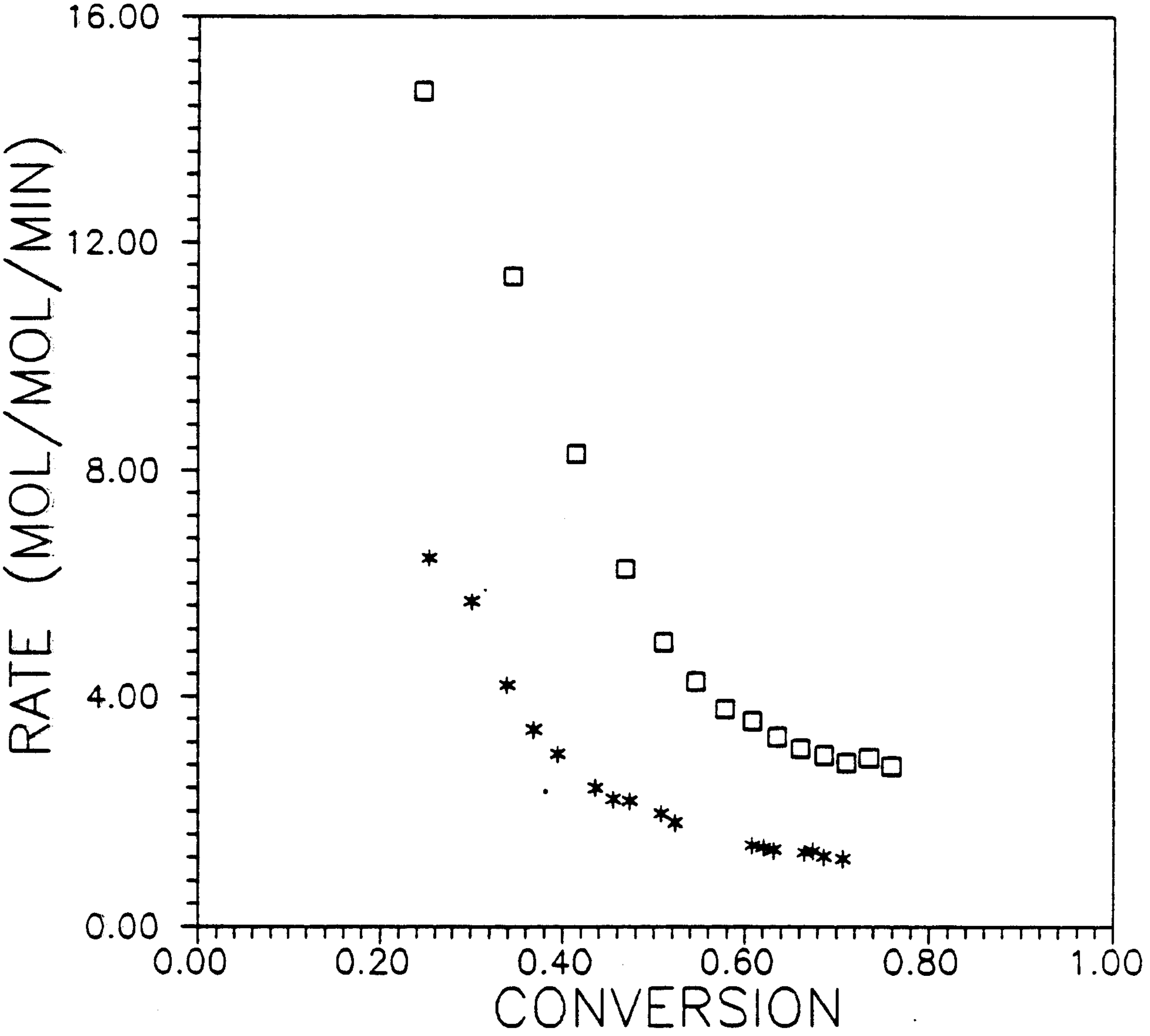
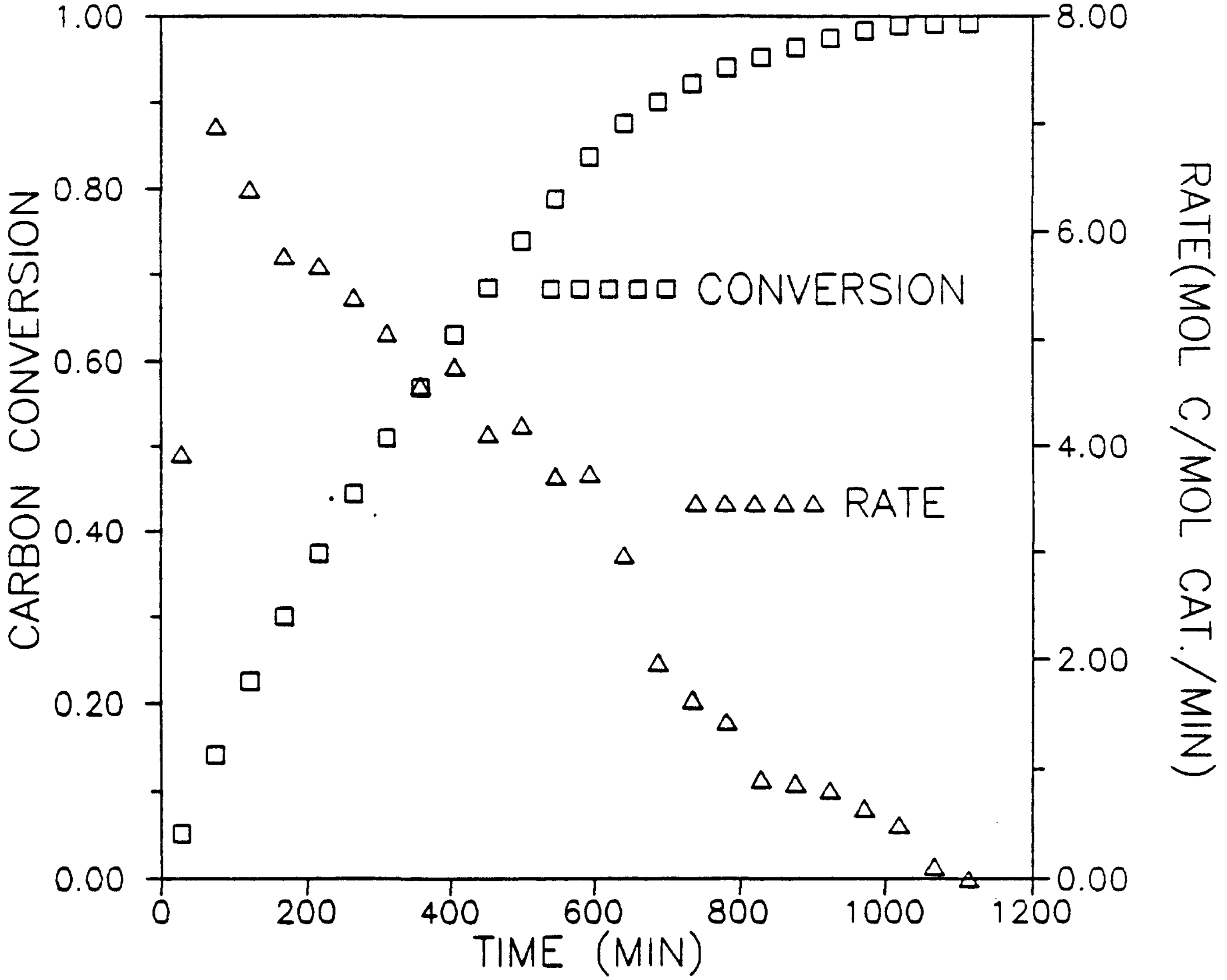

20.00
15.00
10.00
5.00
0.00
RATE (MOL/MOL/MIN)
0.00
0.20
0.40
0.60
0.80
1.00
CONVERSION
□□□□□ KCaNiOx/ROSEBUD COAL AS RECEIVED
△△△△△ KCaOx/ROSEBUD COAL AS RECEIVED
K/C=0.01,Ca/C=0.01,Ni/C=0.005. STANDARD CONDITIONS.

Fig. 2



***** $KNiO_x$/FRANKLIN COAL AS RECEIVED
□□□□□ $KCaO_x$/FRANKLIN COAL AS RECEIVED
KCa/C=0.01, KNi/C=0.01, STANDARD CONDITIONS

Fig. 3



$CsBaO_x$/FRANKLIN COAL AS RECEIVED. STANDARD CONDITIONS

Fig. 4

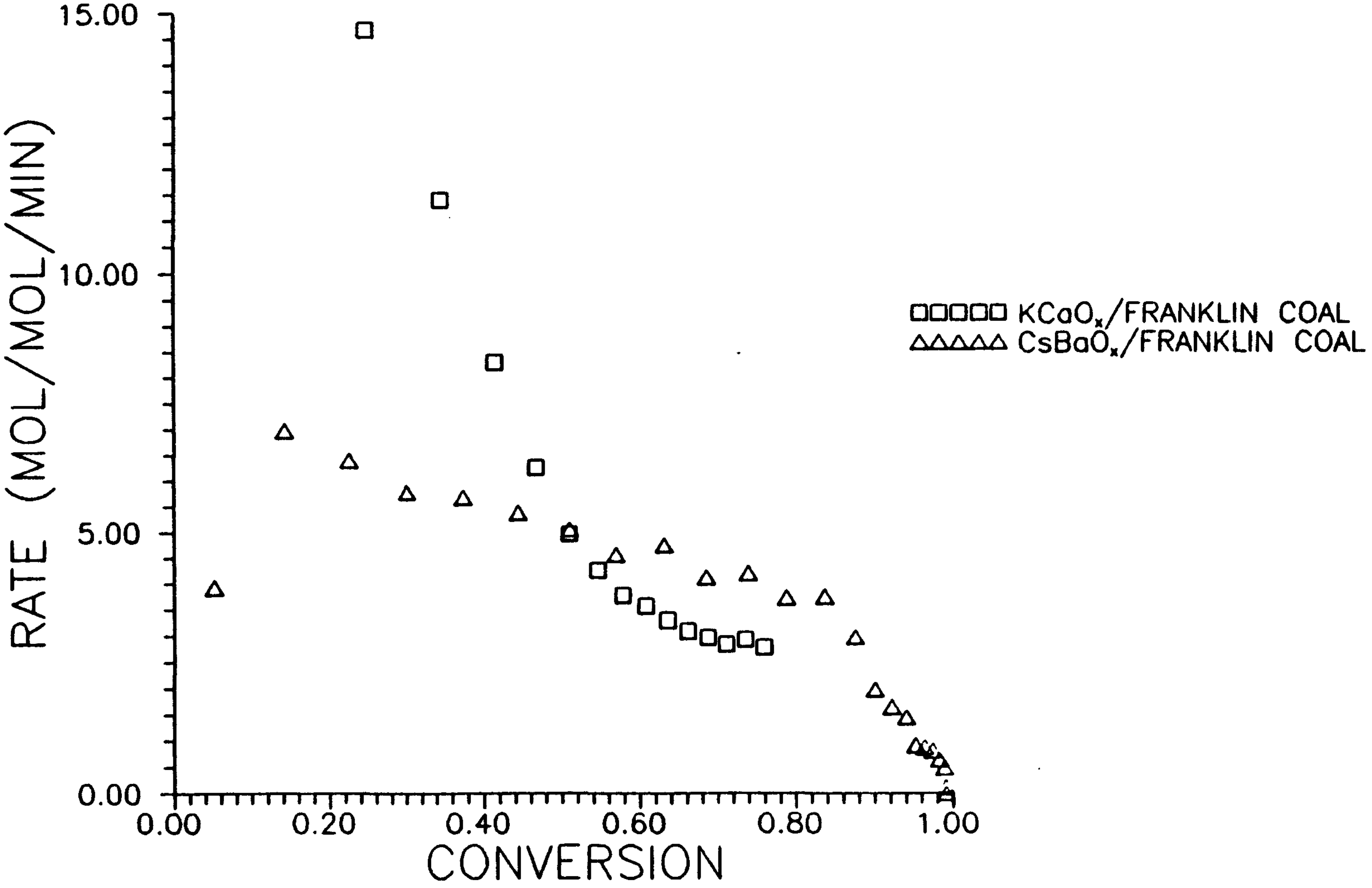
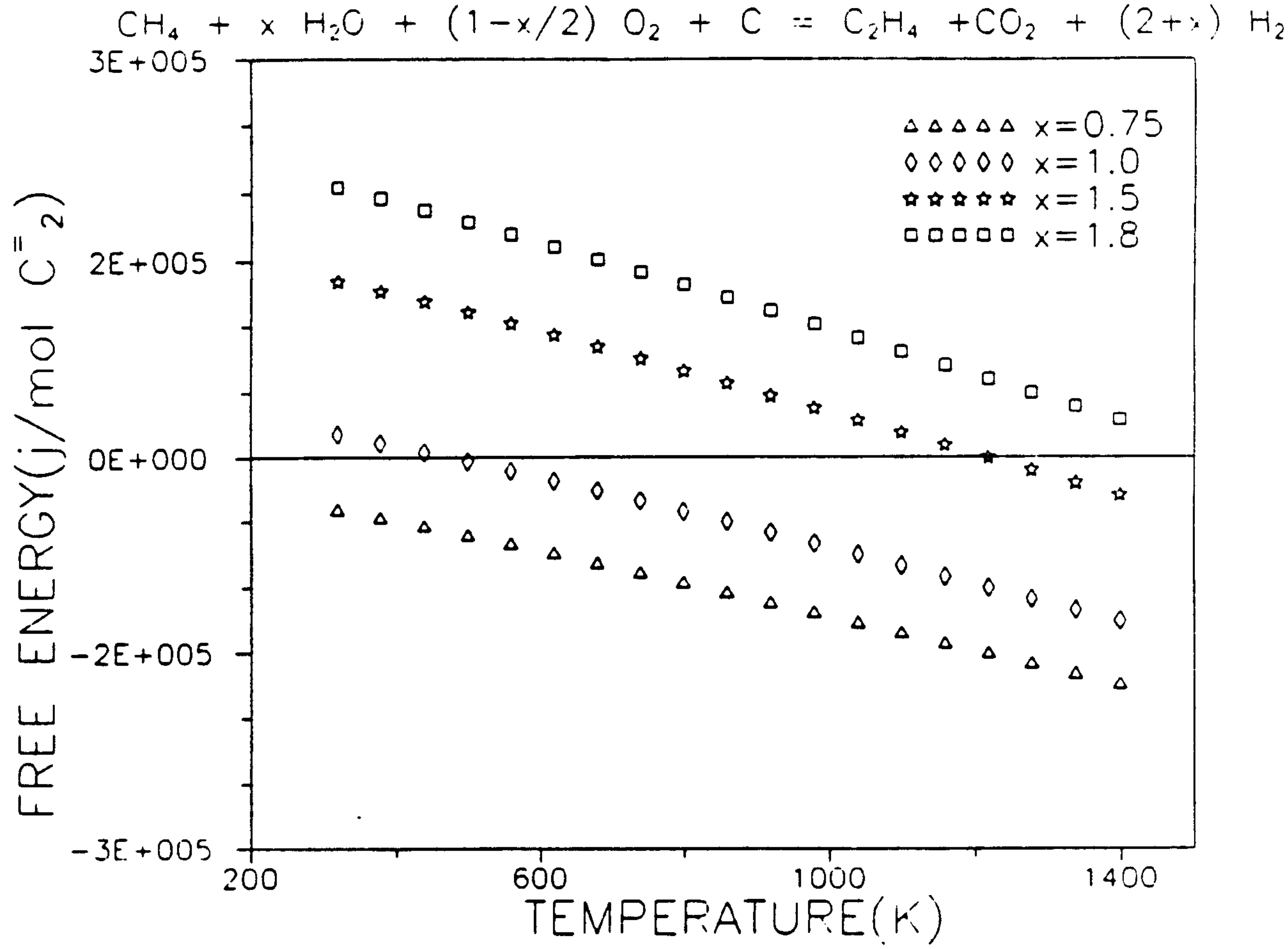

15.00
10.00
5.00
0.00
0.00
0.20
0.40
0.60
0.80
1.00
RATE (MOL/MOL/MIN)
CONVERSION
□□□□□ KCaO$_x$/FRANKLIN COAL
△△△△△ CsBaO$_x$/FRANKLIN COAL

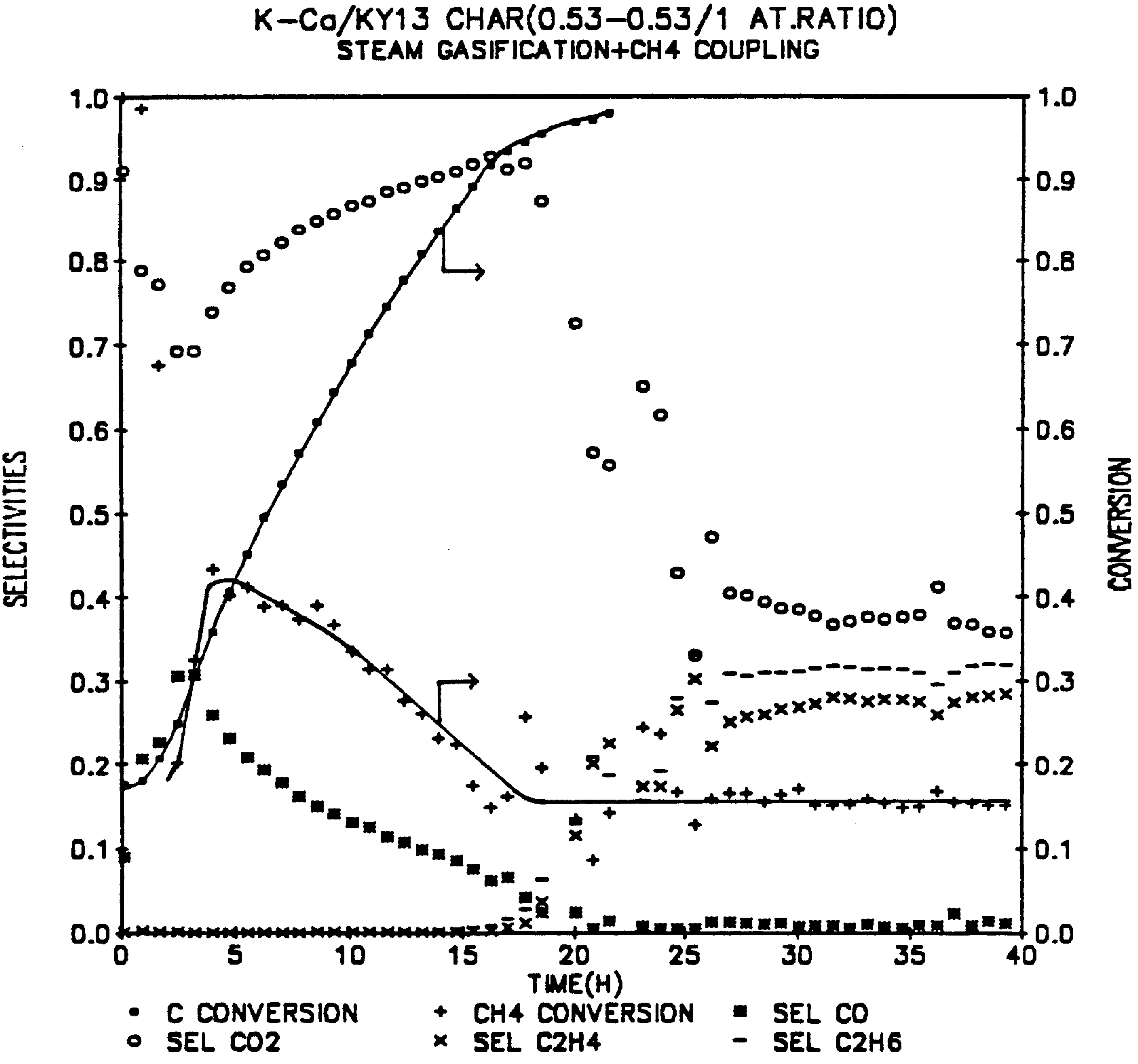
Fig. 5



STANDARD FREE ENERGY EVOLUTION AS A FUNCTION OF TEMPERATURE FOR A HYPOTHETICAL REACTION INVOLVING METHANE, CARBON, STEAM, AND OXYGEN

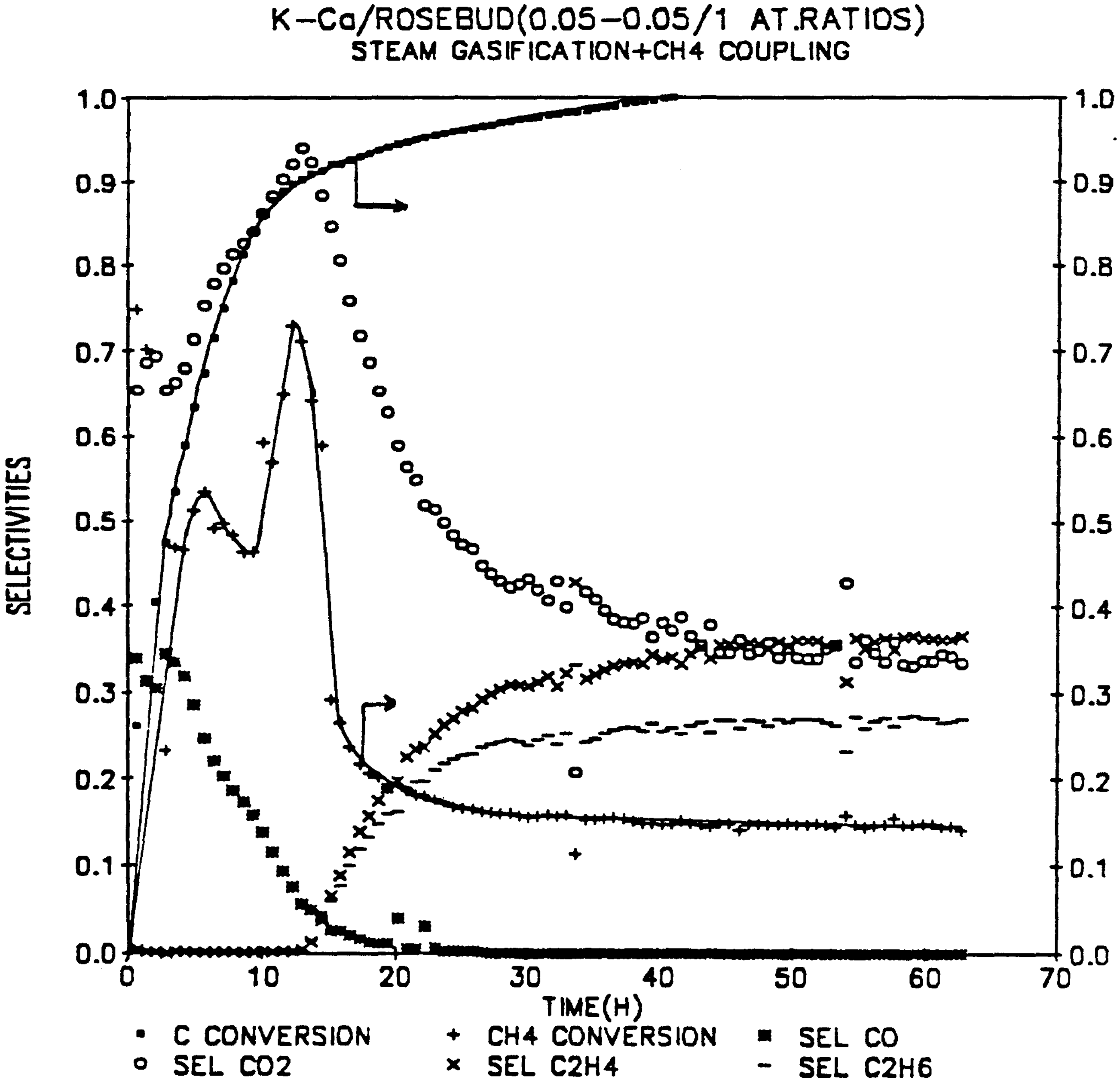
Although the reaction is formally a combination of methane coupling and steam carbon gasification, the thermodynamics suggest that excessively high temperatures are not required for methane coupling if the pathway involves a carbon-like intermediate.

Fig. 6



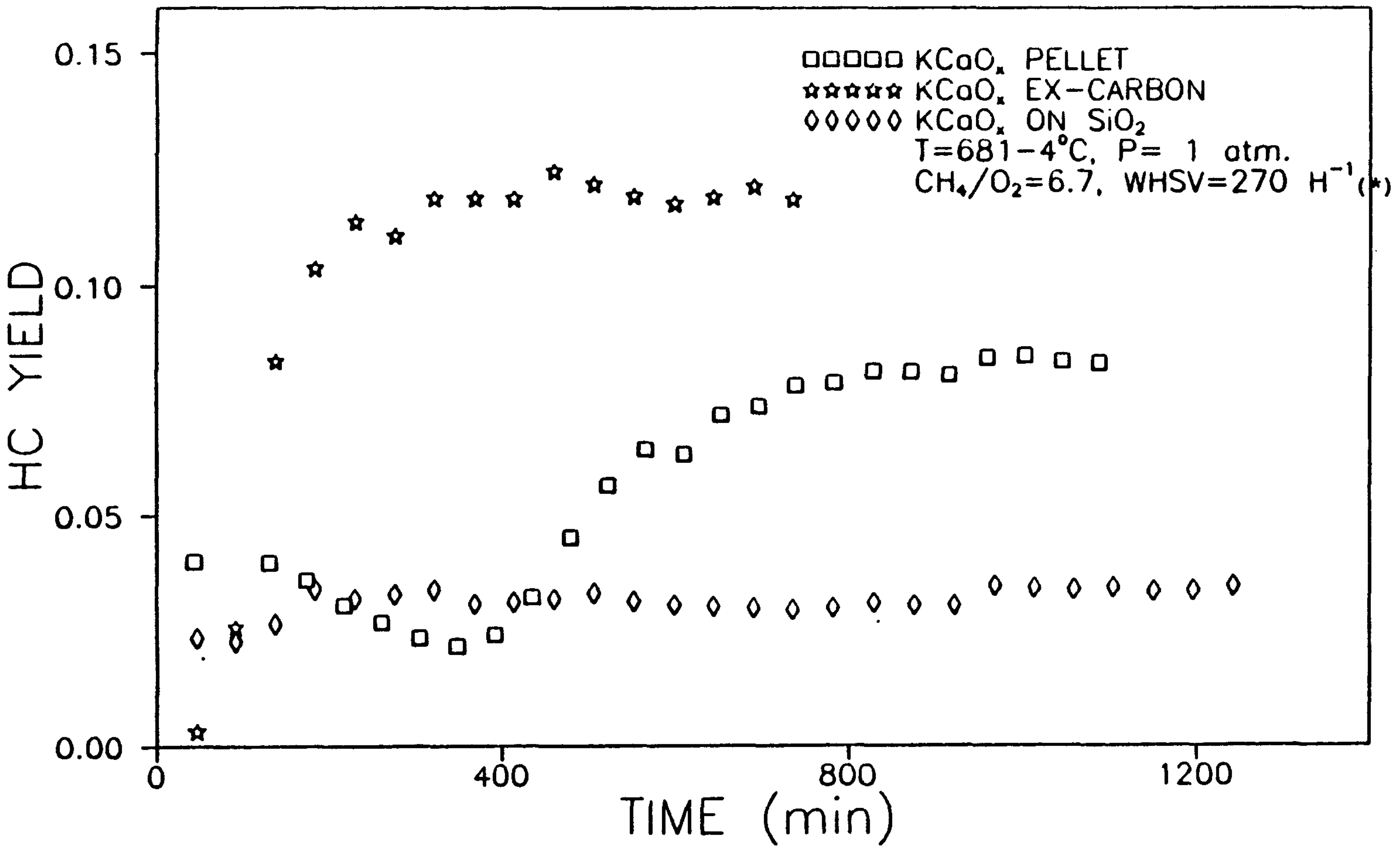
CONDITIONS:T=685°C, P=1 ATM , CH4/O2=6 , WVHSV:270 H^{-1}
HYDROCARBONS YIELD @ 40 HOURS= 9.6%

Fig. 7



CONDITIONS: T=685°C, P=1 ATM , $CH_4/O_2=6$, WVHSV: 270 H^{-1}
HYDROCARBONS YIELD @ 60 HOURS = 10.1%

Fig. 8



(*) WATER, METHANE AND OXYGEN FLOWS WERE ADJUSTED FOR EACH CASE IN ORDER TO KEEP CONSTANT THE SPACE VELOCITY

Fig. 9

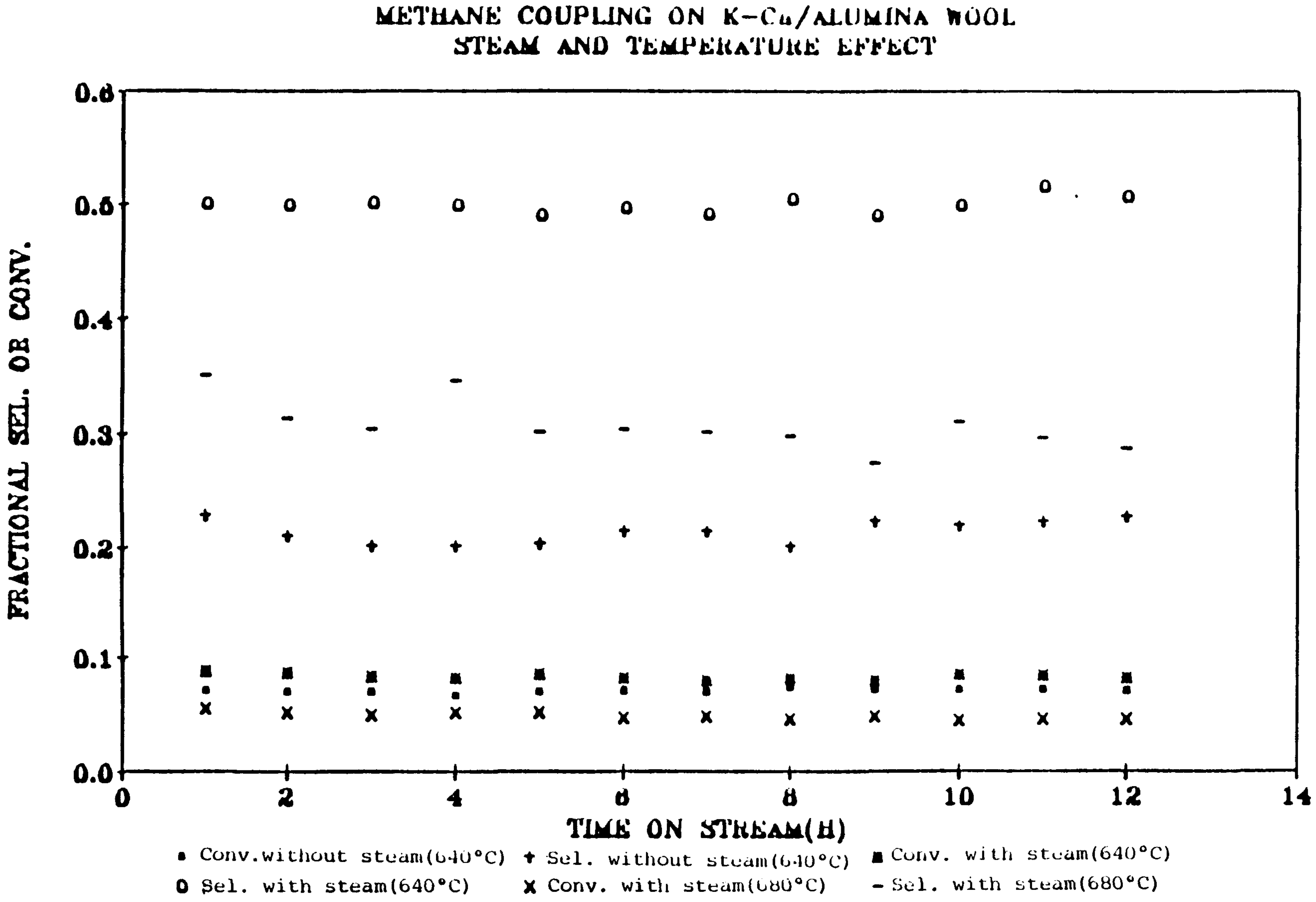

METHANE COUPLING ON K-Cu/ALUMINA WOOL
STEAM AND TEMPERATURE EFFECT
FRACTIONAL SEL. OR CONV.
0.8
0.6
0.4
0.3
0.2
0.1
0.0
0
2
4
6
8
10
12
14
TIME ON STREAM(H)
• Conv.without steam(640°C)
+ Sel. without steam(640°C)
■ Conv. with steam(640°C)
O Sel. with steam(640°C)
X Conv. with steam(680°C)
– Sel. with steam(680°C)

Fig. 10

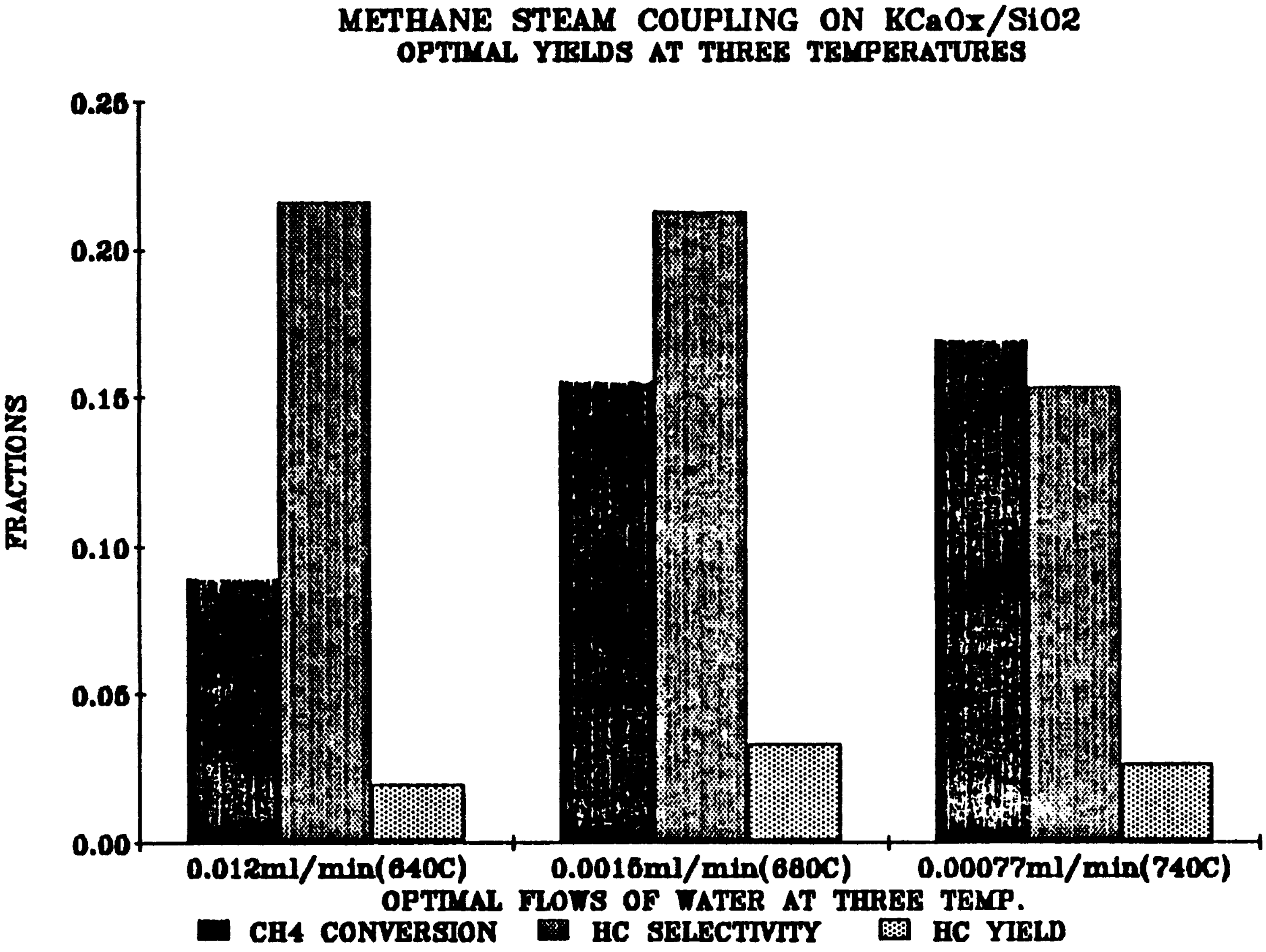
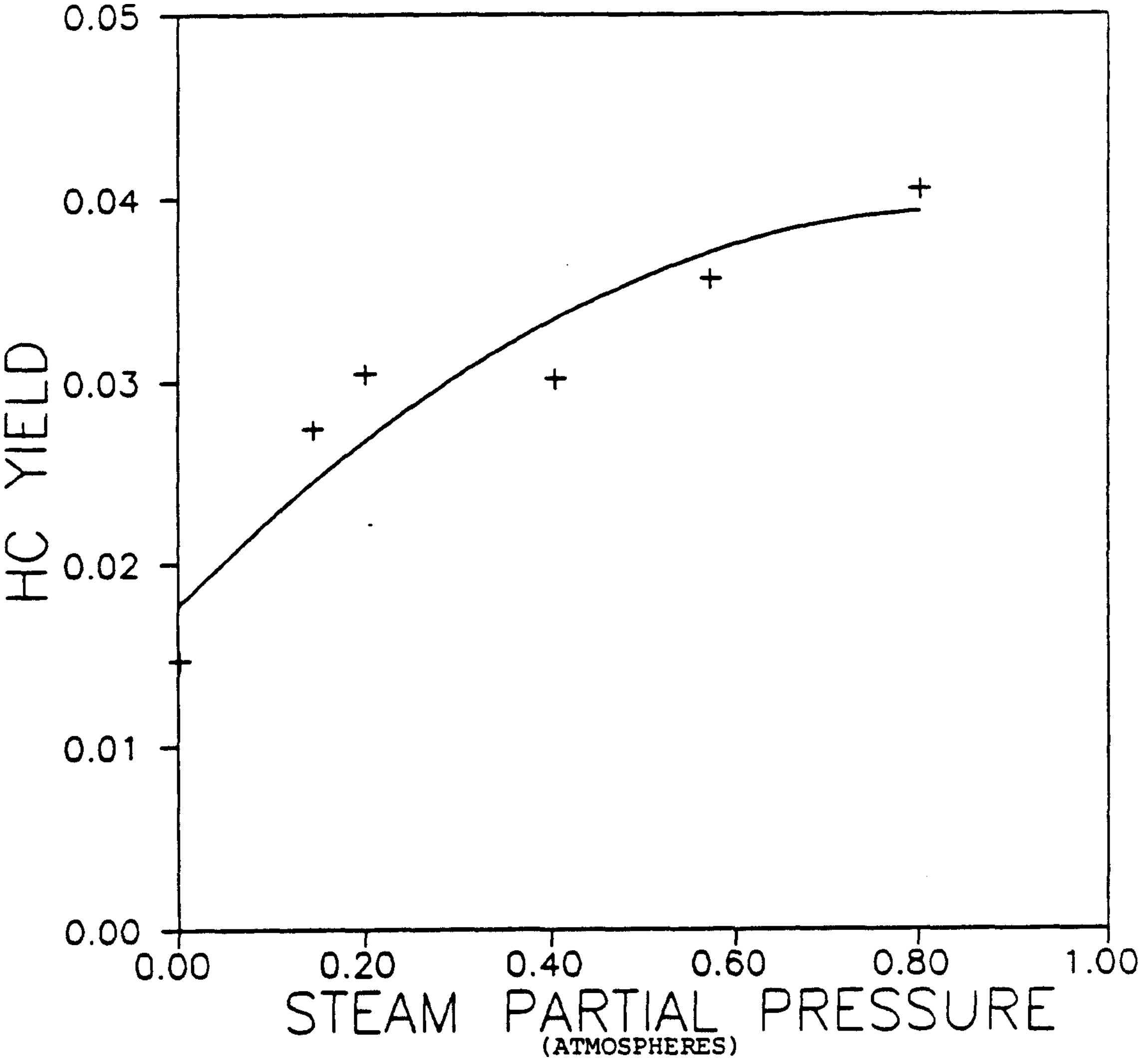

METHANE STEAM COUPLING ON KCaOx/SiO2
OPTIMAL YIELDS AT THREE TEMPERATURES
FRACTIONS
0.25
0.20
0.15
0.10
0.05
0.00
0.012ml/min(640C)
0.0015ml/min(680C)
0.00077ml/min(740C)
OPTIMAL FLOWS OF WATER AT THREE TEMP.
CH4 CONVERSION
HC SELECTIVITY
HC YIELD

Fig. 11



Yield dependance of the water partial pressure (atm) for a catalyst KCa/SiO_2
Temp=680°C, a He stream was used to keep total pressure constant.
Fixed flows of CH_4 and O_2 were used to maintain a ratio CH_4/O_2=6.5

Fig. 12