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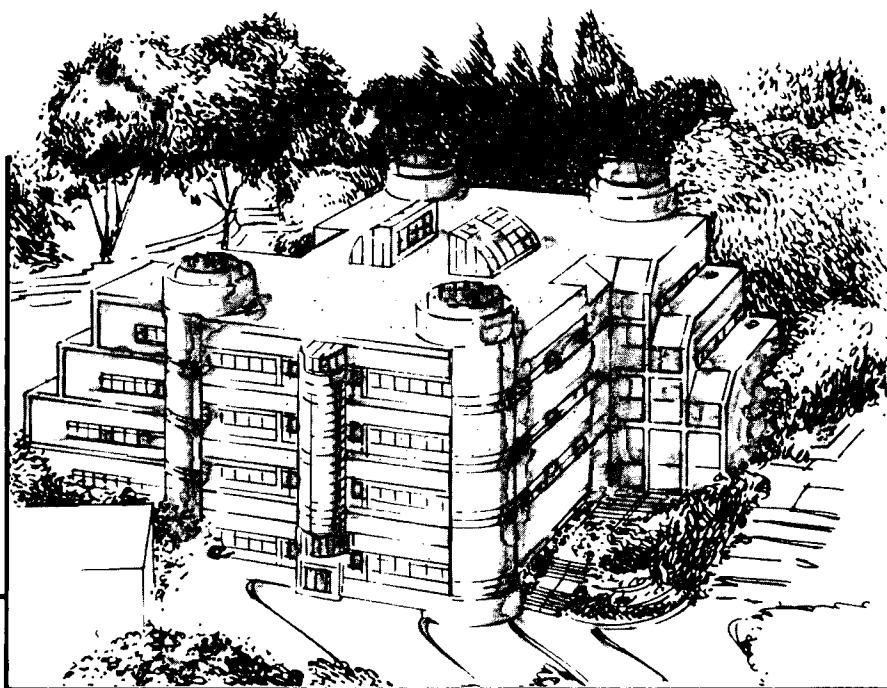
Fundamental Studies of Catalytic Gasification

Quarterly Report

July 1–September 30, 1991

H. Heinemann and G.A. Somorjai

September 1991



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QUARTERLY REPORT

July 1, 1991 - September 30, 1991

**FUNDAMENTAL STUDIES OF CATALYTIC
GASIFICATION**

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I. Task Description for FY 1991

STUDIES OF THE CATALYTIC STEAM GASIFICATION OF CARBON SOLIDS

In this project a considerable number of important findings have been made. Leads for scale-up have been developed and mechanisms for the reaction have been delineated. A small amount of additional experimental work is necessary and the extensive body of this project must be summarized in a final report. Recently limited experimentation has been carried out on the production of C₂ hydrocarbons from methane in the presence of Ca/K/Ni oxide catalysts and of oxygen, carbon and water. The main finding thus far has been that C₂ yields of 10-13% can be obtained at about 600°C or 150° lower temperature than described in the literature for similar yields. Occasionally much higher yields were obtained and reasons for this must be determined. We have recently found that with a modified catalyst and by operating at quite low temperature (≈600°C) CO₂ formation can be almost totally suppressed. Yields of 7-10% C₂ hydrocarbons at 99+% selectivity have been obtained. The presence of water and small amounts of oxygen is essential. Yields of this magnitude may be attractive since there is no loss of methane to valueless by-products, no purification of the recycle steam is required and no oxygen is used to burn methane. Further improvement in yields by catalyst and operating conditions modification will be investigated. It is also intended to clarify the chemistry which inhibits burning of methane to carbon oxides.

II. Introduction

A summary report *Fundamental Studies of Catalytic Gasification* has been published by LBL (LBL-30015; UC-109). It contains a review of several years' work on this project and summarizes numerous journal publications as well as LBL quarterly reports.

A paper on oxidative methane coupling has been published in CATALYSIS LETTERS 9, 395-402 (1991). This paper was appended in draft form to the July 1, 1991, quarterly report (LBL-30816).

A CRADA has been completed between LBL and ACT Orion USA on future collaboration on oxidative methane coupling starting October 1, 1991. The CRADA is now awaiting final DOE approval.

The current report covers extensive work on low temperature catalytic oxidative coupling of methane at relatively low temperatures and high hydrocarbon selectivities, carried out during the July-September 1991 quarter.

III. Highlights

a) Catalytic Steam Gasification of Coals

- A summary report of several years' work has been issued (LBL-30015).
- Invention studies for potential patent applications have been submitted.

b) Oxidative Methane Coupling

- To clarify the reaction mechanism, isotope experiments were carried out using D₂O, ¹³CH₄ and H₂¹⁸O. With D₂O and H₂¹⁸O no isotopes were found in either hydrocarbon or CO_x products. Water, though essential for

the reaction, does not participate in its chemistry but apparently affects the catalyst. When $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$ were used in charging methane, oxygen and water to a CaNiK oxide catalyst, using a helium purge between $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$, $^{13}\text{CO}_2$ was observed while charging $^{12}\text{CH}_4$. This indicates carbon deposition on the catalyst during reaction, possibly as a reaction intermediate.

- Calculations show that oxidative coupling over CaNiK oxide catalysts is a catalytic rather than a stoichiometric reaction.
- CaNiK oxide catalysts are active for methane coupling only when pretreated with O_2 or O_2 and H_2O at temperatures of 680°C or higher. If pretreated at lower temperatures, they are oxidation or steam reforming catalysts.
- The effect of the ratio of water to CH_4 and O_2 on catalyst performance has been investigated at constant 3:1 CH_4 and O_2 ratio and flow. In the absence of water only carbon oxides are formed. At very high water ratios high selectivity was initially observed but it declined rapidly with corresponding CO_2 formation. The optimum ratio of $\text{CH}_4:\text{O}_2:\text{H}_2\text{O}$ is about 3:1:6.
- An investigation of the effect of contact time showed that the longest contact time investigated (≈ 50 sec) gave the best hydrocarbon selectivity. Short contact times (≈ 12 sec) resulted in increasing conversion and CO_2 selectivities.
- The role of oxygen concentration in the feed was explored. In the absence of oxygen at extremely low conversion ($<1\%$), initially about 80% CO_2 and 20% hydrocarbons were produced, probably due to oxygen adsorbed or contained in the catalyst. The highest hydrocarbon selectivity ($>95\%$) was initially obtained at about a molar $\text{CH}_4:\text{O}_2:\text{H}_2\text{O}$ ratio of 9:1:6.5 but this selectivity gradually declined. Hydrocarbon selectivity was constant at $\approx 92\%$ for 7-10 hours at a $\text{CH}_4:\text{O}_2:\text{H}_2\text{O}$ ratio of 3:1:6.5. At higher oxygen concentration ($\text{CH}_4:\text{O}_2:\text{H}_2\text{O} = 1:1:6.5$) CO_2 selectivity dominated.
- Catalysts containing other transition metals than Ni were prepared and tested. A $\text{Ca}_3\text{Co}_1\text{K}_{0.1}$ catalyst gave about 7% conversion and initially 90% hydrocarbon selectivity, but this selectivity declined quite rapidly. A $\text{Ca}_3\text{Fe}_1\text{K}_{0.1}$ catalyst showed low conversion and a dramatic decline in hydrocarbon selectivity after initial high selectivity.
- Substitution of magnesium oxide for calcium oxide in the catalyst resulted in an essentially inactive coupling and very active CO_2 producing catalyst, even when run at lower temperatures.

- The role of CO_2 as a deactivating agent (by formation of CaCO_3) was again investigated. A CaCO_3 -Ni-K oxide catalyst (Ca:Ni:K = 3:1:0.1) was prepared and calcined in O_2 at 680°C (well below the 900°C CaCO_3 decomposition temperature). This catalyst gave 70-80% selectivity to hydrocarbons for about 10 hours, indicating that the often observed sudden rate of decline of selectivity for a $\text{Ca}_3\text{Ni}_1\text{K}_{0.1}$ catalyst from >90% to <50% after 6-10 hours operation is not likely due to surface carbonate formation.

IV. Progress of Studies

a) Effect of catalyst ($\text{Ca}_3\text{Ni}_1\text{K}_{0.1}$) pretreatment

The results are summarized in Table 1. High temperature (680°C) is necessary for obtaining an active and selective catalyst. At this temperature pretreatment with O_2 , H_2O (He), and ($\text{H}_2\text{O} + \text{O}_2$) resp. leads to a good catalyst. After any other pretreatments at 600°C and below, only total oxidation and/or steam reforming reactions were observed.

The high temperature seems to form an active and selective surface species on the catalyst, which is probably an O^- surface species.

b) Effect of water in the feed on catalyst activity and selectivity

In a series of experiments, the ratio of $\text{CH}_4:\text{O}_2$ and its flow rates were kept constant and the amount of water was varied.

In the absence of water, only carbon oxides were formed (Table 2). Using a reacting mixture of $\text{CH}_4:\text{O}_2:\text{H}_2\text{O} = 3:1:3.3$ (1.5 cc CH_4/min , 0.5 cc O_2/min and 0.0014 cc $\text{H}_2\text{O}/\text{min}$) hydrocarbons were detected only at the very beginning of the reaction and then only carbon oxides were produced.

High and constant hydrocarbon selectivity was observed, however, at the $\text{CH}_4:\text{O}_2:\text{H}_2\text{O} = 3:1:6.5$ reaction mixture. (This is the standard mixture of 1.5 cc CH_4/min , 0.5 cc O_2/min and 0.0027 cc $\text{H}_2\text{O}/\text{min}$, resp.). There was no CO formation in this case.

Further increase of the amount of water in the feed resulted in initially high hydrocarbon selectivity; this gradually decreased with time, with a concomitant increase of CO_2 selectivity. There was no CO among the products.

It is concluded that the catalytic performances of the $\text{Ca}_3\text{Ni}_1\text{K}_{0.1}$ catalyst depends on the amount of water added to the feed. The optimum value was observed at a ratio of $\text{CH}_4:\text{O}_2:\text{H}_2\text{O} = 3:1:6.5$.

c) Effect of total flow rate

The amount of the catalyst in the reactor was increased from the usual 1g to 2g, providing a greater possibility for varying the total flow rate. The ratio of the reactants was kept constant ($\text{CH}_4:\text{O}_2:\text{H}_2\text{O} = 3:1:6.5$). The flow rates of the gases were varied.

Contact times were calculated. The standard contact time is ≈ 23 sec. Other contact times used were 47.1 sec. and 11.7 sec.

The best catalytic performance was observed at the lowest total flow rate or longest contact time. At a conversion of $\approx 7\%$, the hydrocarbon selectivity was above 90%, C_2H_4 , C_3H_6 , C_3H_8 and C_4 s were produced in the greatest amount (Table 3). Doubling the total flow rate gave a conversion of $\approx 5\%$ and hydrocarbon selectivity is 91%; the amount of C_2H_6 is slightly higher, the amounts of other hydrocarbons are slightly smaller than in the previous case. In both cases the catalyst selectivity was constant for at least six hours. When a four time larger flow rate was applied, the conversion and the CO selectivity increased with time, while hydrocarbon selectivity was decreasing. Among hydrocarbons, C_2H_6 was dominant; no C_3H_6 and C_4 were detected.

d) *Effect of oxygen concentration in the feed*

In these experiments the amount of water was kept constant and the flow rates of CH_4 and O_2 were varied, keeping their total flow rate constant (2 cc/min).

$$X = \frac{F_{O_2}}{F_{O_2} + F_{CH_4}}$$

where: X = molar fraction of O_2

F_{O_2} = flow rate of O_2

F_{CH_4} = flow rate of CH_4

In the absence of oxygen (only CH_4 and water in the feed) the conversion was about 1%, and hydrocarbon and CO_2 selectivities were $\approx 20\%$ and $\approx 80\%$ respectively (Table 4). As $X(O_2)$ increased, hydrocarbon selectivity showed a maximum at $X(O_2) = 0.1$ ($CH_4:O_2:H_2O = 9:1:6.5$). Further increase of $X(O_2)$ caused a gradual decrease in hydrocarbon selectivity. The CO_2 selectivity consequently shows a minimum at $X(O_2) = 0.1$, and increased with increasing $X(O_2)$. At $X(O_2) = 0.75$ hydrocarbon selectivity was essentially zero; in this excess of O_2 ($CH_4:O_2:H_2O = 1:3:6.5$) CH_4 is converted into CO_2 . These statements are valid for the early stages of the reaction (data were taken at 120 min. on stream). More detailed information is presented in Figs. 1,2,3,4 where the different performances vs. time have been depicted at each $X(O_2)$. There is only a very narrow range of $X(O_2)$ (≈ 0.1 to 0.5) where high hydrocarbon selectivity can be obtained at reasonable conversions using the $Ca_3Ni_1K_{0.1}$ catalyst.

e) *Deactivation of the Ca-Ni-K-oxide catalysts*

$Ca_3Ni_1K_{0.1}$ catalysts usually loose selectivity fairly quickly after 5-7 hours on stream at high selectivity. After this stable period at high selectivity, there is a decrease in hydrocarbon selectivity and a simultaneous increase in CO_2 selectivity. The conversion is also increased during this period of the reaction.

One of the possible causes for this phenomena could be the formation of surface carbonate (mainly $CaCO_3$) on the catalyst from CO_2 produced during the reaction. Experiments were performed on a $CaCO_3NiK$ catalyst (Ca:Ni:K - 3:1:0.1) similarly prepared and pretreated as the $CaNiKO_x$ catalysts. The highest temperature used in these experiments never exceeded $680^\circ C$.

As can be seen in Fig. 5, this catalyst exhibits a surprisingly high (80-60%) hydrocarbon selectivity for more than 10 hours. The gradual decrease of hydrocarbon selectivity and the simultaneous increase of CO_2 formation can be observed only after 15 hours on stream. From these results it can be inferred that although the presence of surface carbonate affects the hydrocarbon selectivity, the $CaCO_3NiK$ catalyst is not completely inactive in the oxidative methane coupling. Thus the formation of surface carbonate in the reaction would not be a decisive factor for the catalyst's deactivation. The previously deactivated catalysts can be easily regenerated

by an overnight oxidation at 680-700°C at a temperature far below the temperature of decomposition of CaCO_3 . This finding also makes it unlikely that CaCO_3 formation is a cause of deactivation.

f) *Isotope experiments*

Using H_2^{18}O and D_2O respectively we have not observed isotope-containing compounds among the products (i.e., no C^{18}O or C^{18}O_2 , nor D-containing hydrocarbons). Therefore, water does not participate directly in the chemistry of the reaction, although its presence in the feed is essential for having an active and selective catalyst.

In some of these experiments a $^{12}\text{CH}_4\text{-O}_2\text{-H}_2\text{O}$ gas mixture was first introduced to the catalyst; after two hours on stream, the system was purged with He (at 600°C) removing CH_4 and other gases and then a $^{13}\text{CH}_4\text{-O}_2\text{-H}_2\text{O}$ mixture was introduced. In another experiment, the same sequence of the reaction was performed starting with $^{12}\text{CH}_4\text{-O}_2\text{-H}_2\text{O}$ mixture. The products were analyzed by GC/MS.

Only labelled carbon oxides and no labelled hydrocarbons were detected in the second part of these experiments. We have observed ^{12}CO and $^{12}\text{CO}_2$ when using the $^{13}\text{CH}_4\text{-O}_2\text{-H}_2\text{O}$ mixture, and ^{13}CO and $^{13}\text{CO}_2$ when using a $^{12}\text{CH}_4\text{-O}_2\text{-H}_2\text{O}$ mixture in the second part (Fig. 6 and Fig. 7). It appears that carbon deposition occurs during oxidative coupling of CH_4 . After removing the gaseous CH_4 , this deposited carbon produces only carbon oxides in the reacting $\text{CH}_4\text{-O}_2\text{-H}_2\text{O}$ mixture. The carbon deposition may be responsible for the deactivation of the catalysts.

g) *Effect of transition metals in the catalyst*

Catalytic oxidative methane coupling gave different results when other transition metals were substituted for nickel in a $\text{Ca}_3\text{NiK}_{0.1}\text{O}_x$ catalyst operated under identical conditions.

A newly prepared $\text{Ca}_3\text{Ni}_1\text{K}_{0.1}$ catalyst has shown the same high hydrocarbon selectivity (above 90%) and low CO_2 selectivity (under 10%) at a CH_4 - conversion of 10% for 5 hours on stream as previously reported. During the active period of this catalyst, the ratio of $\text{C}_2\text{H}_6\text{:C}_2\text{H}_4$ was approximately 1, and ca. 10% of the total hydrocarbon content of the products was detected as C_3H_6 , C_3H_8 and C_4s . After 5 hours the hydrocarbon selectivity decreased with concomitant increase of CO_2 (Fig. 8).

With a $\text{Ca}_3\text{Co}_1\text{K}_{0.1}$ catalyst the reaction began with high hydrocarbon selectivity (90%) and low CO_2 selectivity (10%). A gradual decrease in hydrocarbon selectivity and a concomitant increase of CO_2 selectivity was observed; however, without any extended period of stability. Ethane and ethylene were the main hydrocarbons ($\text{C}_2\text{H}_6\text{:C}_2\text{H}_4 \approx 2\text{:}1$), and only 6-3% of higher hydrocarbons (C_2H_6 , C_3H_8 and C_4s) was detected. The conversion of CH_4 was of 5-7% (Fig. 8).

The loss in hydrocarbon selectivity and the increase in CO_2 selectivity occurred faster with a $\text{Ca}_3\text{Fe}_1\text{K}_{0.1}\text{O}_x$ catalyst. After 2 hours on stream the hydrocarbon selectivity was only 10% and the main product was CO_2 (90% selectivity). The ratio of ethane:ethylene was 5-6:1, no propylene and C_4 hydrocarbons were observed and only traces of propane was detected. The conversion of CH_4 increased from its original value of 1.5% to 8% and the formation of CO_2 became dominant.

Accordingly, the effectiveness of the transition metals investigated above decreased in the order of $\text{Ni} > \text{Co} > \text{Fe}$. Taking into account the changes in the product distribution, this change

can be connected with the different oxidation ability of these metals to oxidize the unsaturated hydrocarbons mainly C_2H_4 and C_3H_6 on the surface.

h) Experiments with a $Mg_3Ni_1K_{0.1}$ catalyst

For comparison some experiments were made with a $Mg_3Ni_1K_{0.1}$ catalyst. The preparation, the pretreatment, and the experimental conditions were the same as in the case of $Ca_3Ni_1K_{0.1}$ catalysts.

At $600^\circ C$ a conversion of 40% was observed but except for the very beginning of the reaction (15 min) only carbon oxides and hydrogen were detected (Table 5). In view of the high conversion, it seemed worthwhile to investigate the catalytic performances of this catalyst at lower temperatures. (In the case of a $Ca_3Ni_1K_{0.1}$ catalyst it had previously been shown that lowering the temperature leads to the reduction of CO_x formation with the concomitant increase of hydrocarbons though at lower conversion.)

As can be seen in Table 5, with a $Mg_3Ni_1K_{0.1}$ catalyst carbon dioxide forms even at 550 and $500^\circ C$. As the conversion at $500^\circ C$ was only 5%, further decrease of the temperature would not be interesting.

$Mg_3Ni_1K_{0.1}$ catalyst therefore did not cause CH_4 coupling. Steam reforming and oxidation of CH_4 occurs at $600^\circ C$; at lower temperatures (550 and $500^\circ C$ resp.) oxidation of CH_4 was observed.

i) Turnover frequency and turnover number of methane coupling on $Ca_3Ni_1K_{0.1}$

It is worthwhile to calculate the turnover frequency (number of transformed molecules on one surface site/sec) and turnover number (number of transformed molecules on the surface site during the active period of this site) in order to determine whether a reaction is catalytic or homogeneous.

In our case the calculation is a severe underestimate of the turnover numbers. We cannot measure the number of active surface sites. We have, therefore, assumed in the following calculation that each surface site is active in CH_4 coupling, which is obviously not the case. As the number of active sites should be much smaller than the total number of surface sites, the turnover frequency and turnover should be higher than calculated below.

The surface area of a pretreated $Ca_3NiK_{0.1}$ catalyst is $0.794 \text{ cm}^2/\text{g}$. Supposing the number of surface sites of 1 m^2 is to be 10^{19} , we have 0.794×10^{19} surface sites on the catalyst.

1) Variation A

We have observed a 10% conversion; i.e., $0.15 \text{ cc } CH_4/\text{min}$ has been converted (the flow rate of CH_4 is $1.5 \text{ cc}/\text{min}$); this amounts to 6.72×10^{18} CH_4 molecules converted/sec.

Turnover frequency: $6.72 \times 10^{18} / 0.794 \times 10^{19} = 8.46 \times 10^{-3} \text{ molecules/sec}$. If the active period of the catalyst is 300 min (18000 sec), the turnover number is $8.46 \times 10^{-3} \times 18000 = 152 \text{ molecules/site}$.

2) Variation B

Based upon the results of an experiment, we have calculated the turnover frequency and the turnover number from the amount of product molecules. The turnover frequency: $5.6 \times 10^{-3} \text{ molecules/sec/site}$

The turnover: 101 molecules/site.

It is generally accepted that if the turnover number is larger than 1, the reaction is catalytic rather than stoichiometric. Our reaction is therefore catalytic.

TABLE 1
The Effect of Pretreatment^a

Catalyst	Pretreatment	Conversion	Selectivity for					HC Sel	CO ₂ Sel	CO Sel
			C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄ +			
Ca ₃ NiK _{0.1}	Fresh catalyst heated up to 600°C in O ₂	1.78%	-	-	-	-	-	-	100%	-
Ca ₃ NiK _{0.1}	Oxygen at 600°C, 18 hrs	24.18%	-	0.18%	-	-	-	0.18%	66.12%	33.7%
Ca ₃ NiK _{0.1}	Oxygen at 680°C, 18 hrs	9.89%	40.2%	44.4%	3.3%	4.2%	1.6%	93.7%	6.3%	-
Ca ₃ NiK _{0.1}	(H ₂ O+O ₂), 680°C, 18 hrs	8.44%	29.5%	52.4%	2.0%	4.9%	2.7%	91.6%	8.4%	-
Ca ₃ NiNa _{0.5}	H ₂ O(He), 600°C, 18 hrs	63.2%	-	-	-	-	-	-	57.5%	42.5%
Ca ₃ NiNa _{0.5}	Oxygen at 680°C, 18 hrs	4.1%	22.3%	63.1%	1.0%	3.3%	0.5%	90.2%	9.8%	-
Ca ₃ NiNa _{0.5}	H ₂ O(He), 680°C, 18 hrs	8.1%	29.4%	54.2%	2.1%	4.8%	1.2%	91.7%	8.3%	--

^aTemperature: 600°C; the composition of the reacting gas mixture: CH₄:O₂:H₂O = 3:1:6.5;
data obtained at 120 min of the reaction

TABLE 2

The Effect of Water to (Methane + Oxygen) Ratio at 600°C^a

Composition of Feed (C ₂ H ₄ :O ₂ :H ₂ O)	Time on Stream (min)	Methane Conversion (%)	Hydrocarbon Sel. (%)	CO ₂ Sel. (%)	CO Sel. (%)
3:1:0	55	28.3	0.5	53.2	46.3
	290	26.1	0.3	43.2	56.5
3:1:3.3	50	3.0	30.4	69.6	0
	250	25.9	0	63.8	36.2
3:1:6.5	60	6.6	94.7	5.3	0
	290	5.8	90.4	9.6	0
3:1:13.3	40	6.6	85.0	15.0	0
	240	8.9	44.0	56.0	0

^aCatalyst: Ca₃NiK_{0.1}

TABLE 3

The Effect of Total Flow Rate on CH₄ Coupling at 600°C^a

Contact Time (sec)	Methane Conversion (%)	Hydrocarbon Sel. (%)	CO ₂ Sel. (%)	C ₂ H ₄ Sel. (%)	C ₂ H ₆ Sel. (%)	C ₂ H ₆ /C ₂ H ₄
47.1	6.25	94.9	5.1	29.4	56.1	1.91
23.4	4.7	91.4	8.6	22.8	62.7	2.75
11.7	5.1	39.5	60.5	6.6	31.5	4.77

^aCatalyst: Ca₃NiK_{0.1}; data were taken at 120 min on stream

TABLE 4
The Effect of CH₄:O₂ Ratio at Constant H₂O on CH₄ Coupling at 600°C^a

Composition of the feed (CH ₄ :O ₂ :H ₂ O)	Fraction of O ₂ ^b	Methane Conversion %	Hydrocarbon Selectivity (%)	CO ₂ Selectivity (%)	C ₂ H ₄ Selectivity (%)	C ₂ H ₆ Selectivity (%)	C ₂ H ₆ /C ₂ H ₄
3:0:6.5	0	0.8	17.6	82.3	2.6	15.0	5.77
9:1:6.5	0.1	4.3	92.4	7.6	23.7	61.5	2.59
3:1:6.5	0.25	6.8	83.9	16.1	25.2	50.2	1.99
1:1:6.5	0.5	6.7	76.6	23.4	23.9	48.0	2.00
1:3:6.5	0.75	28.6	0.4	99.6	0.2	0.2	1.00

^aCatalyst: Ca₃NiK_{0.1}; data were taken at 120 min on stream

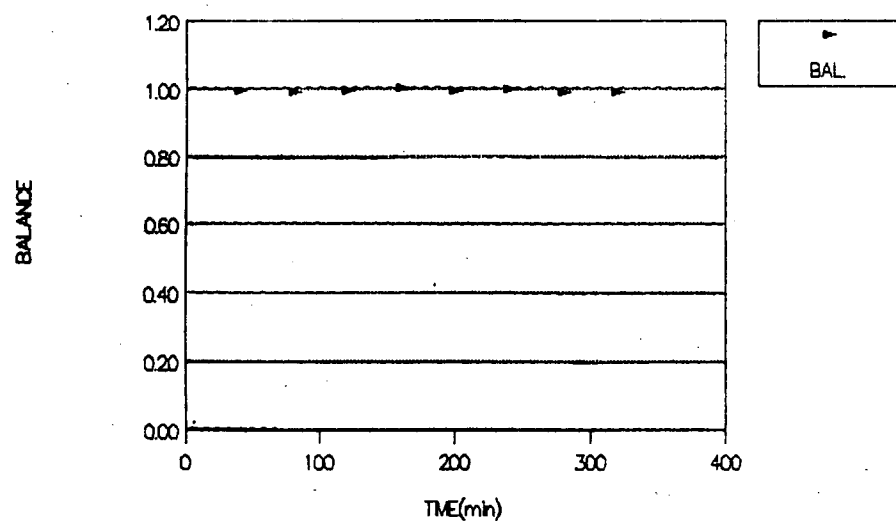
^bCalculated as: $F_{O_2} / (F_{O_2} + F_{CH_4})$ where F_{O_2} = flow rate of O₂ and F_{CH_4} = flow rate of CH₄. ($F_{O_2} + F_{CH_4}$) was kept constant (2cc/min).

TABLE 5
Characteristic Data of CH₄ Coupling
on Mg₃NiK_{0.1} Catalyst

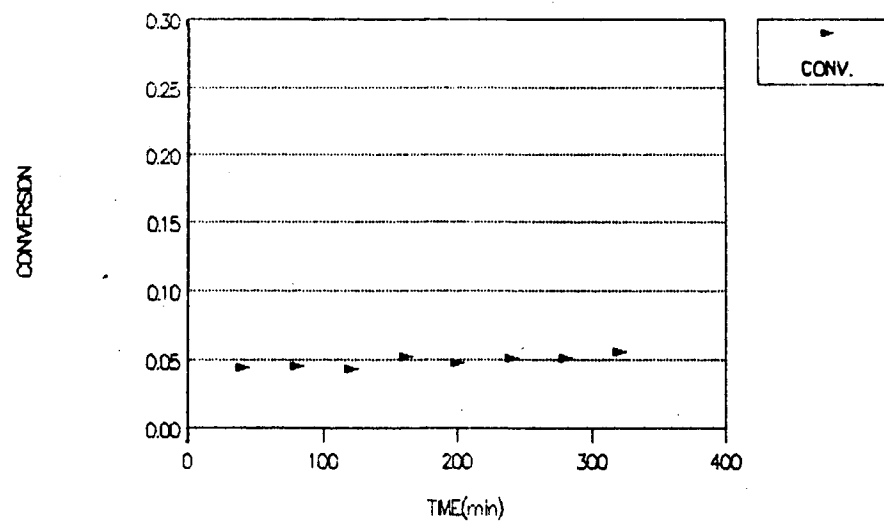
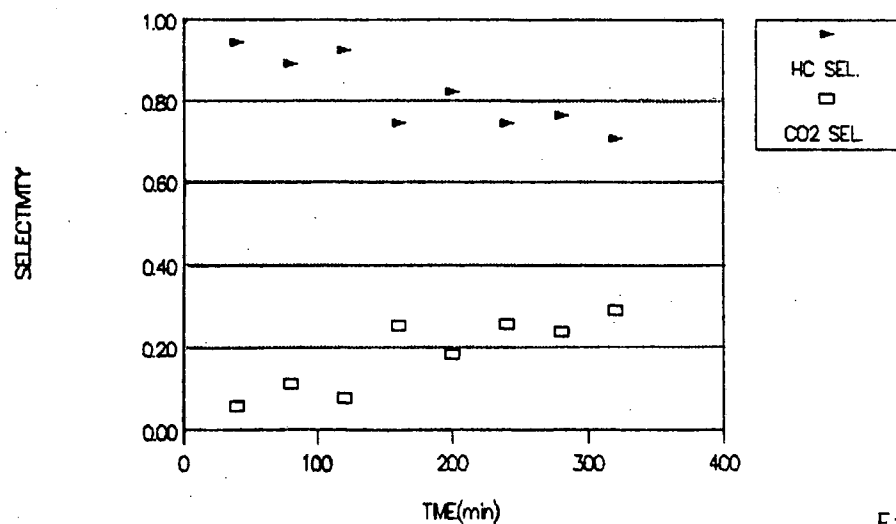
Temperature	Time (min)	Conversion (%)	Hydrocarbon selectivity (%)	CO _x selectivity (%)
500°C	65	4.86	0	100
	300	5.17	0	100
550°C	50	11.9	1.2	98.8
	250	6.2	0.6	99.4
600°C	55	41.0	0	100
	245	38.3	0	100

CH₄:O₂:H₂O=9:1:6.5 on Ca₃NiK_{0.1} at 600CCH₄:O₂:H₂O=9:1:6.5 on Ca₃NiK_{0.1} at 600C

Balance vs. time



Conversion vs. time

CH₄:O₂:H₂O=9:1:6.5 on Ca₃NiK_{0.1} at 600CCH₄:O₂:H₂O=9:1:6.5 on Ca₃NiK_{0.1} at 600CHC and CO₂ sel. vs. time

Sel. of diff. HC vs. time

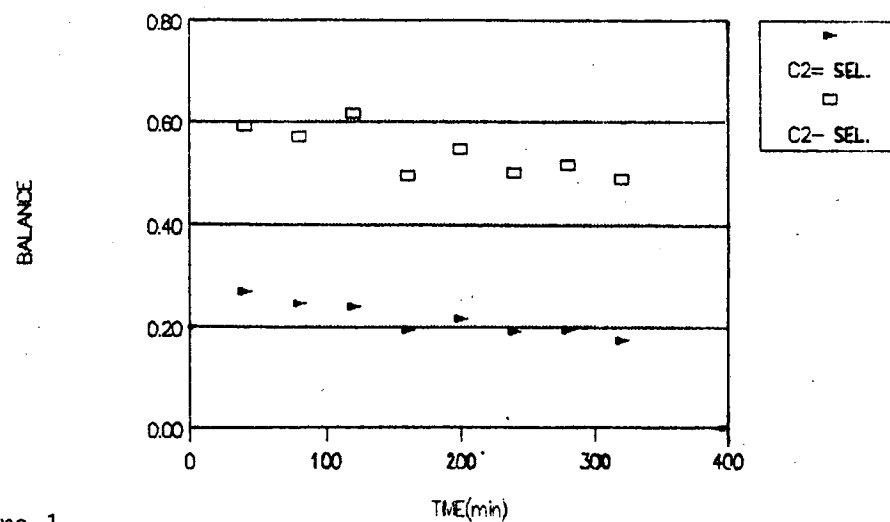


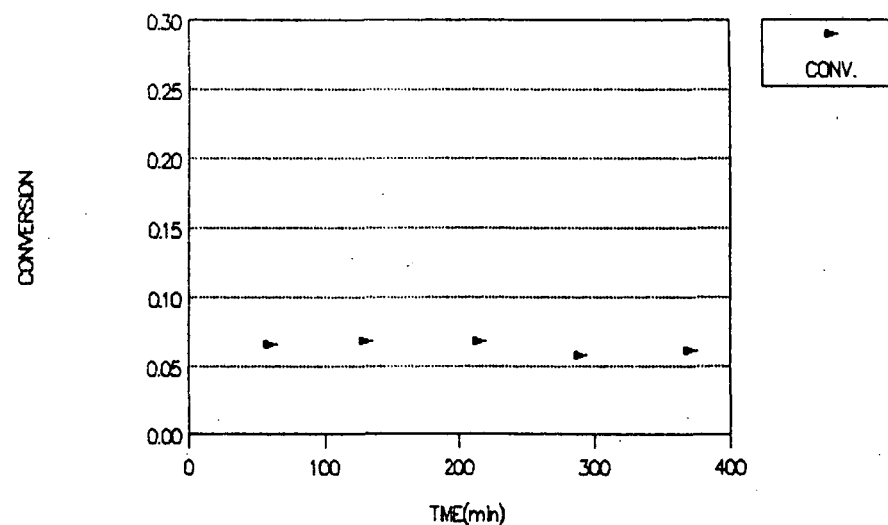
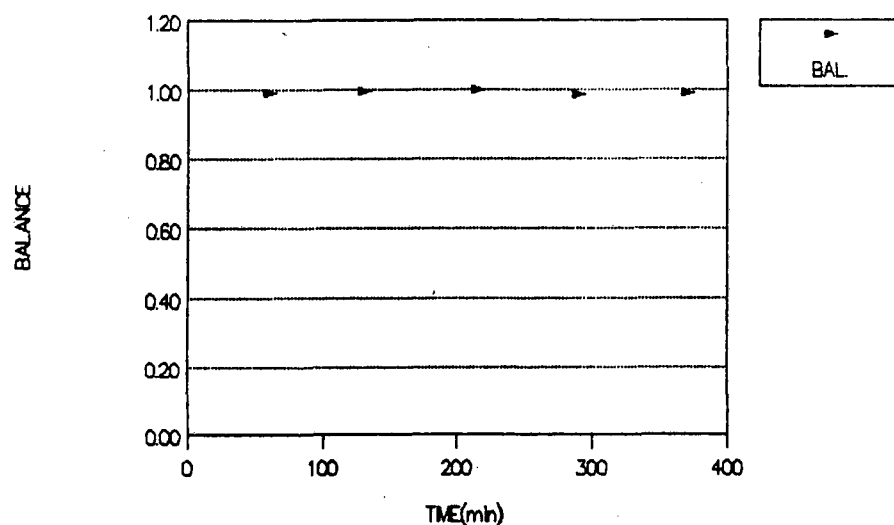
Figure 1

CH₄:O₂:H₂O=3:1:6.5 on Ca₃NiK_{0.1} at 600C

CH₄:O₂:H₂O=3:1:6.5 on Ca₃NiK_{0.1} at 600C

Balance vs. time

Conversion vs. time



CH₄:O₂:H₂O=3:1:6.5 on Ca₃NiK_{0.1} at 600C

CH₄:O₂:H₂O=3:1:6.5 on Ca₃NiK_{0.1} at 600C

HC and CO₂ sel. vs. time

Sel. of diff. HC vs. time

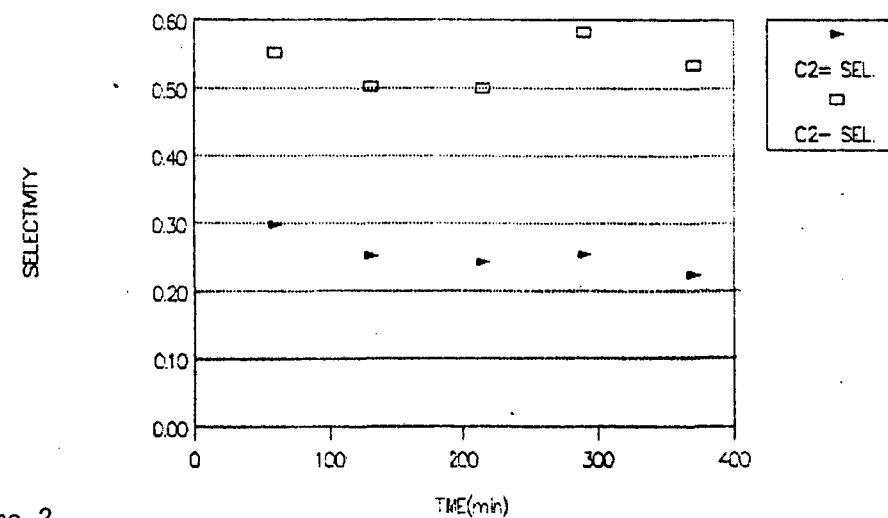
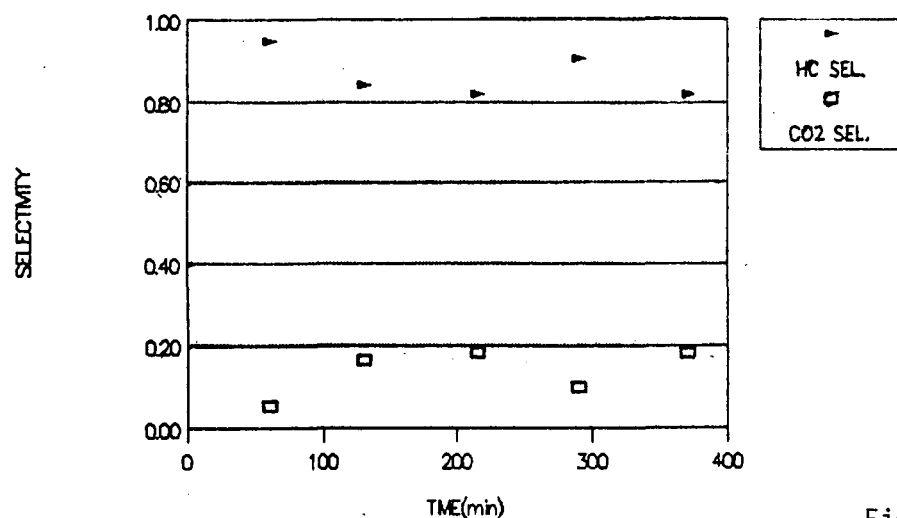
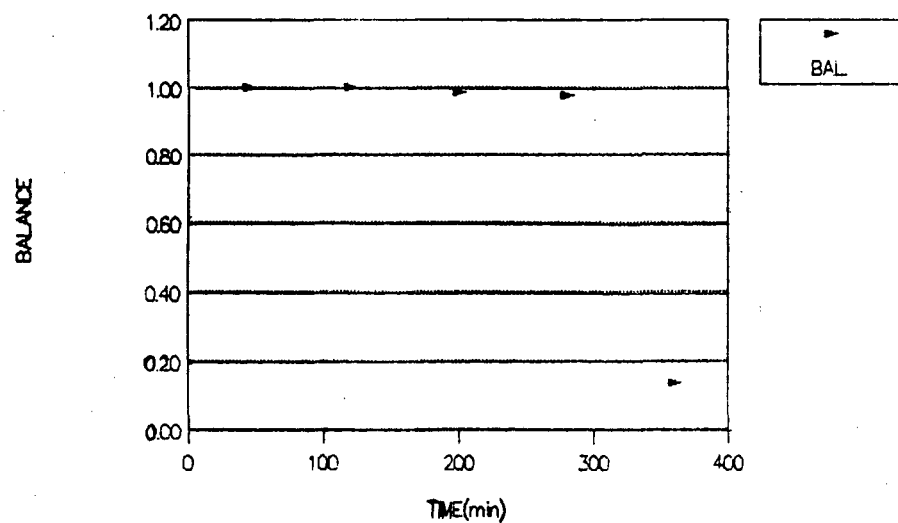


Figure 2

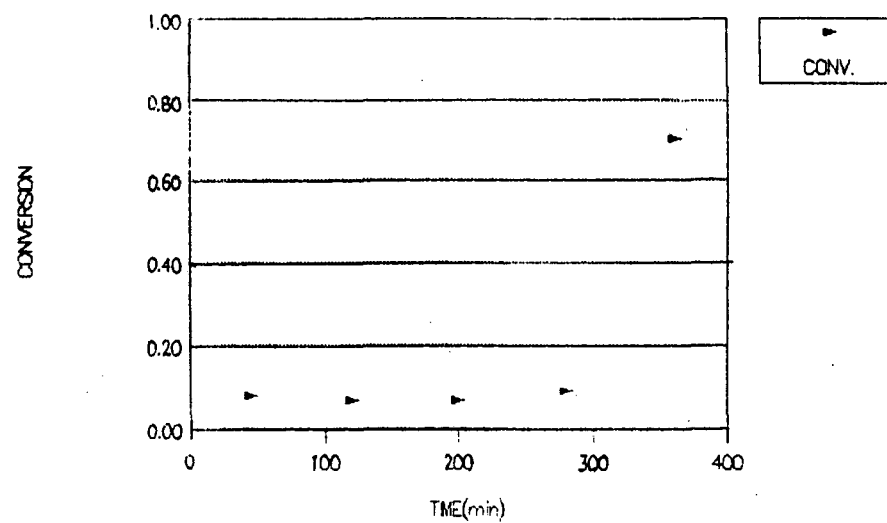
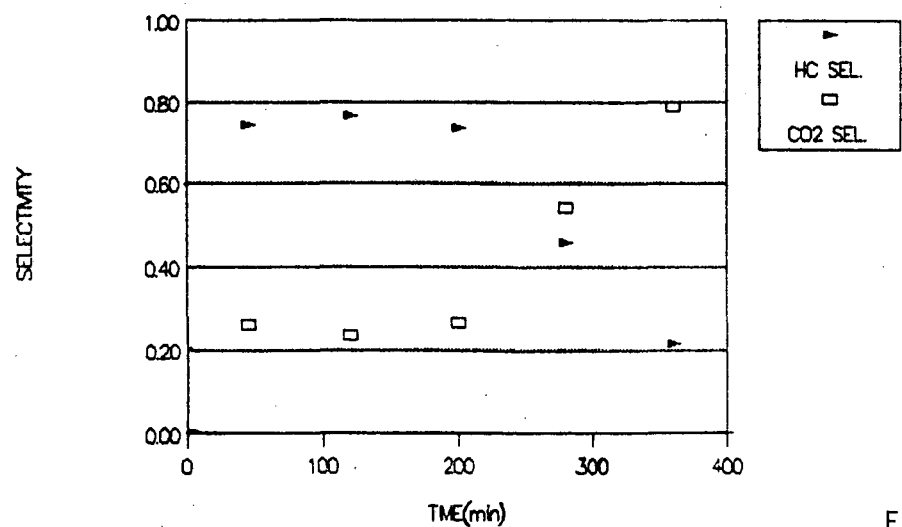
CH₄:O₂:H₂O=1:1:6.5 on Ca₃NiK_{0.1} at 600CCH₄:O₂:H₂O=1:1:6.5 on Ca₃NiK_{0.1} at 600C

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Balance vs. time



Conversion vs. time

CH₄:O₂:H₂O=1:1:6.5 on Ca₃NiK_{0.1} at 600CCH₄:O₂:H₂O=1:1:6.5 on Ca₃NiK_{0.1} at 600CHC and CO₂ sel. vs. time

Sel. of diff. HC vs. time

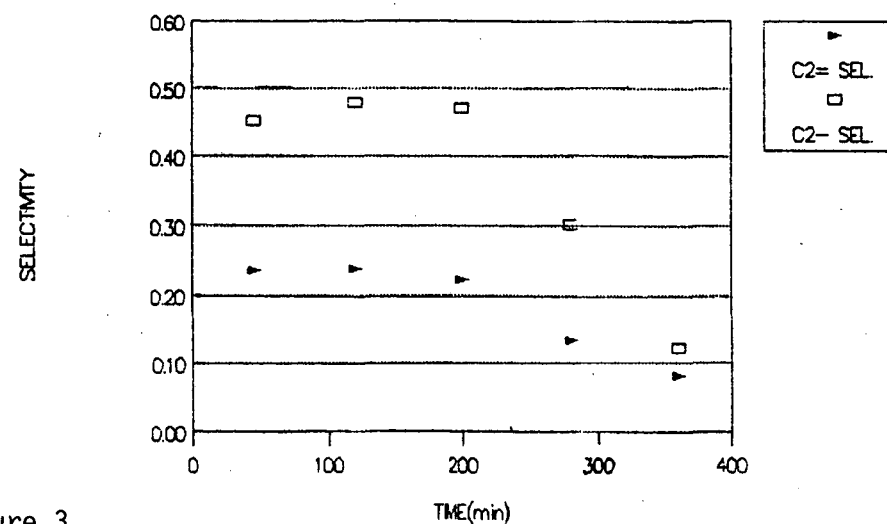


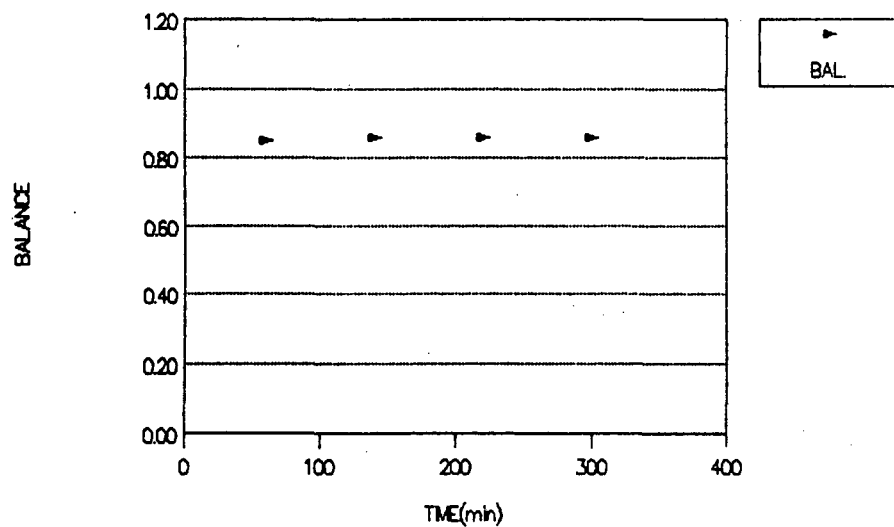
Figure 3

CH₄:O₂:H₂O=1:3:6.5 on Ca₃NiK_{0.1} at 600C

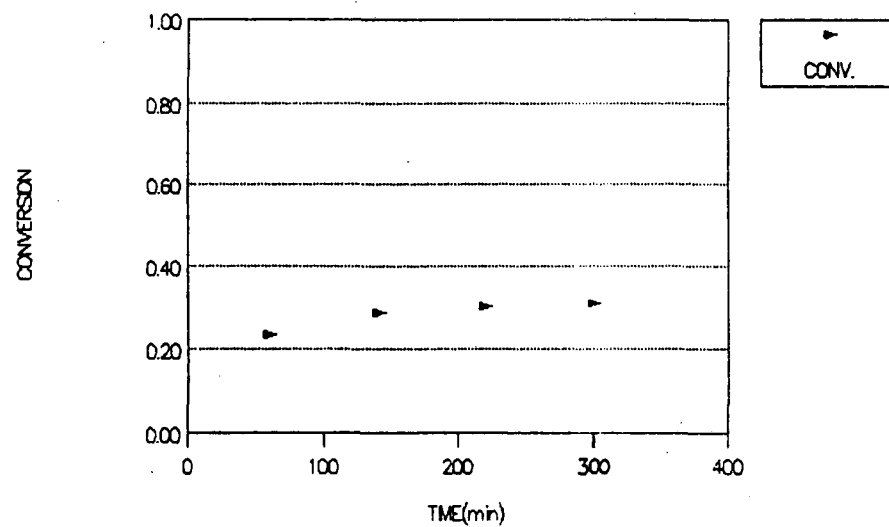
CH₄:O₂:H₂O=1:3:6.5 on Ca₃NiK_{0.1} at 600C

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Balance vs. time



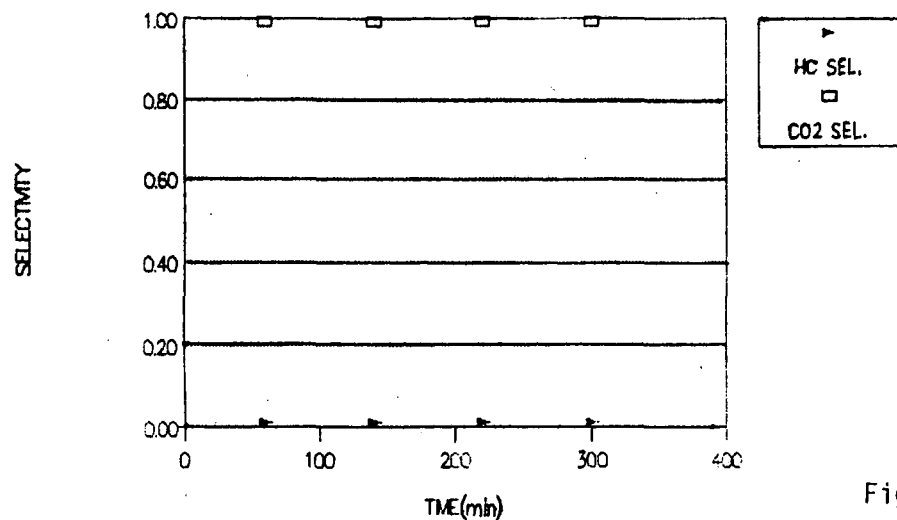
Conversion vs. time



CH₄:O₂:H₂O=1:3:6.5 on Ca₃NiK_{0.1} at 600C

CH₄:O₂:H₂O=1:3:6.5 on Ca₃NiK_{0.1} at 600C

HC and CO₂ sel. vs. time



Sel. of diff. HC vs. time

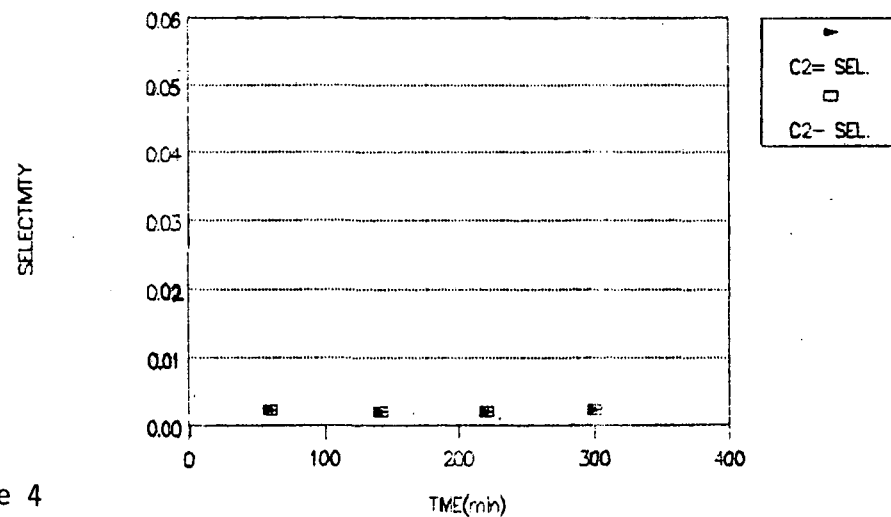


Figure 4

CH₄ COUPLING ON Ca₃(CO₃)NiK_{0.1}(ox.)

HC and CO₂ selectivity vs. time

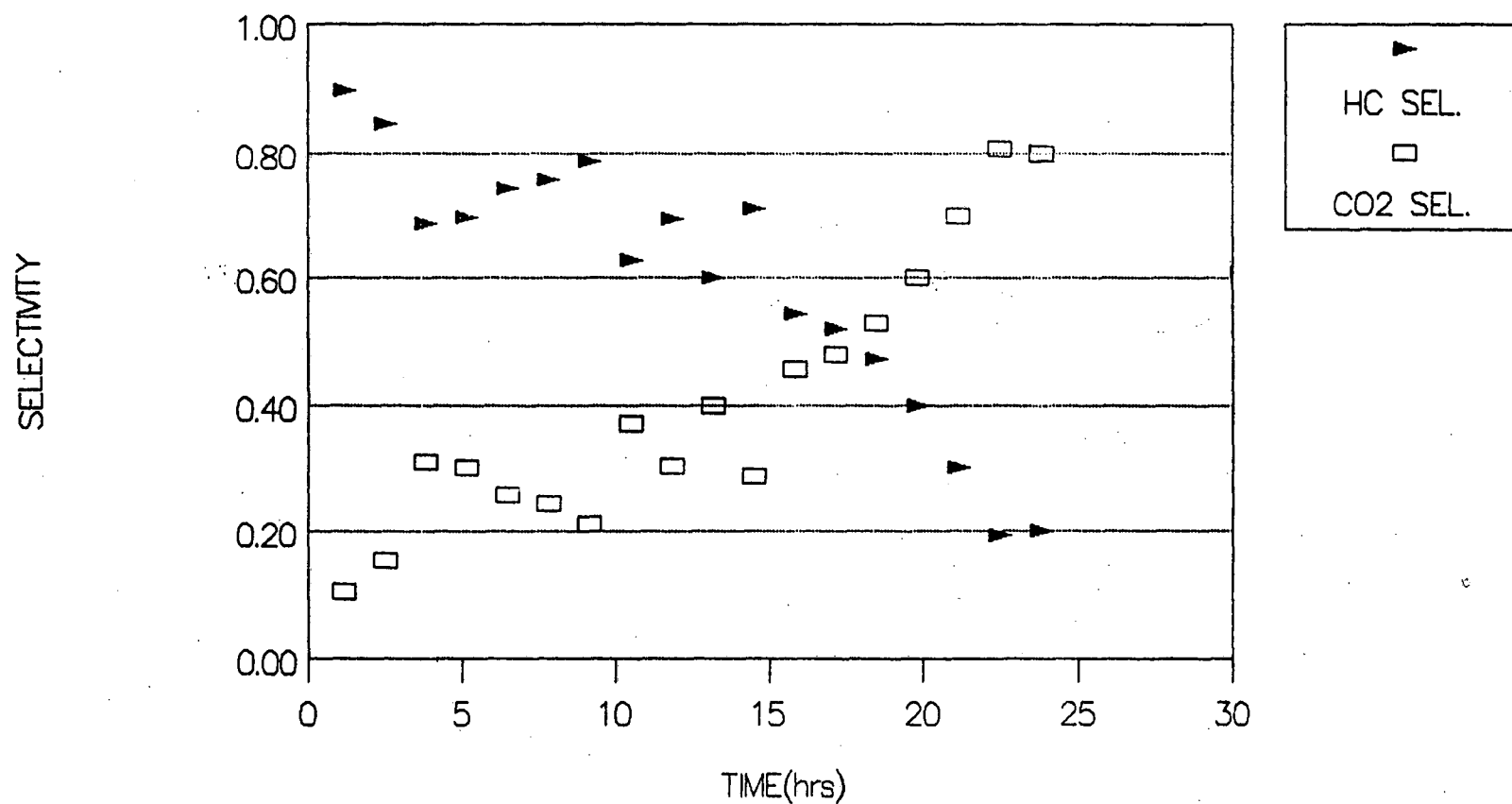


Figure 5

^{12}C – ^{13}C EXCHANGE on $\text{Ca}_3\text{NiK}_{0.1}$ at 600C

Abundance of diff. MS-peaks vs. time

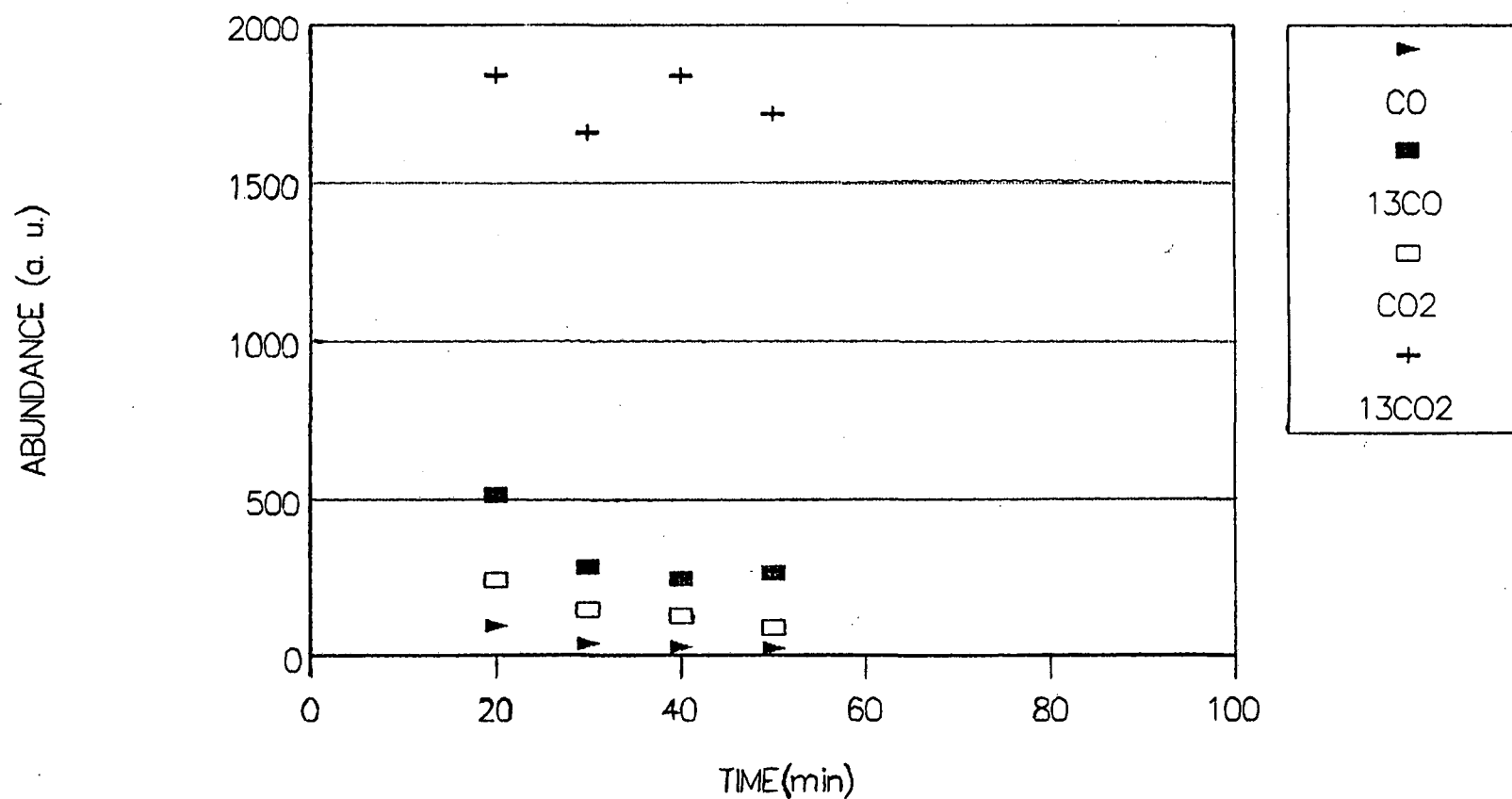


Figure 6

^{13}C – ^{12}C EXCHANGE on $\text{Ca}_3\text{NiK}_{0.1}$ at 600C

Abundance of diff. MS-peaks vs. time

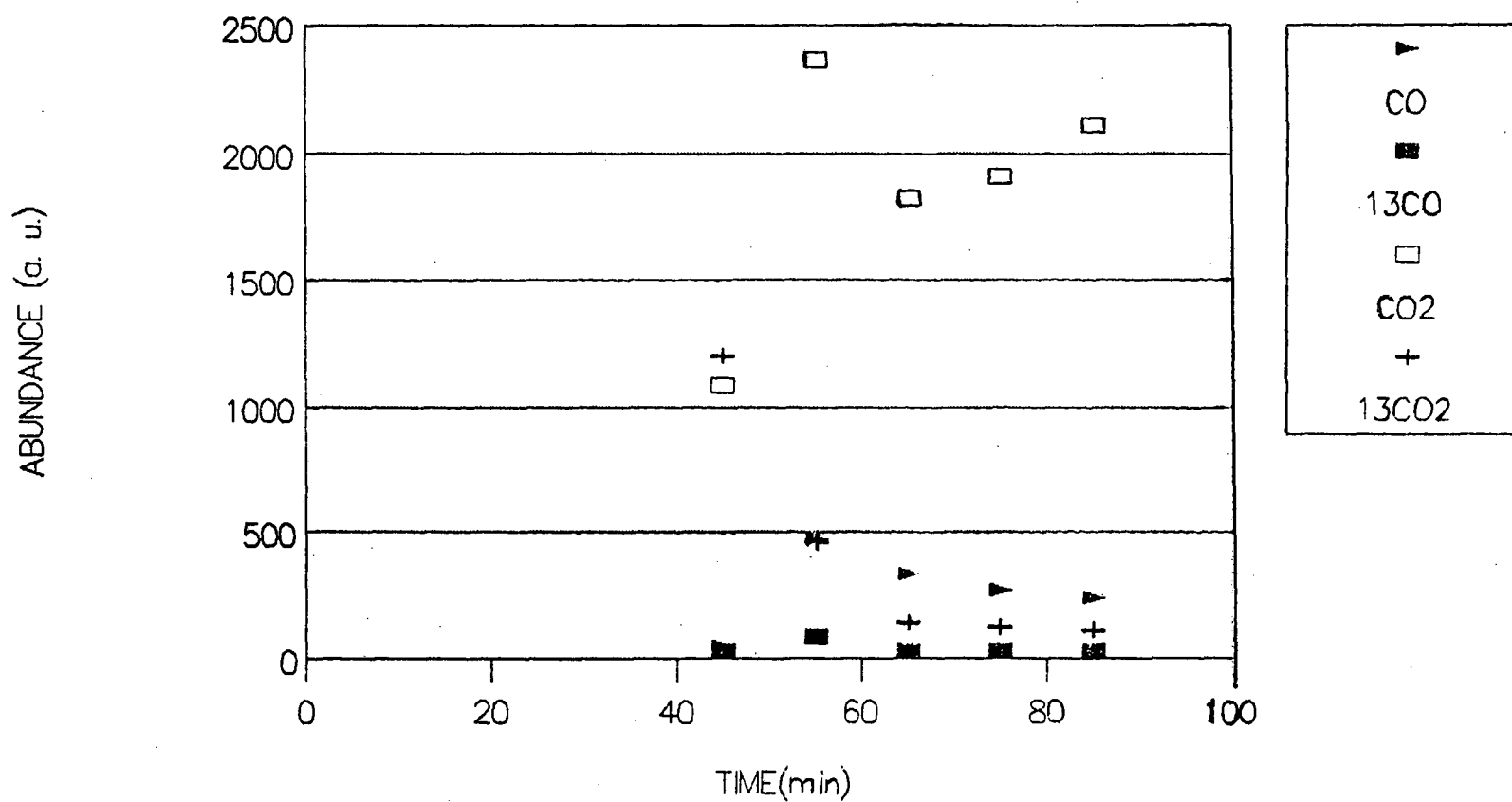


Figure 7

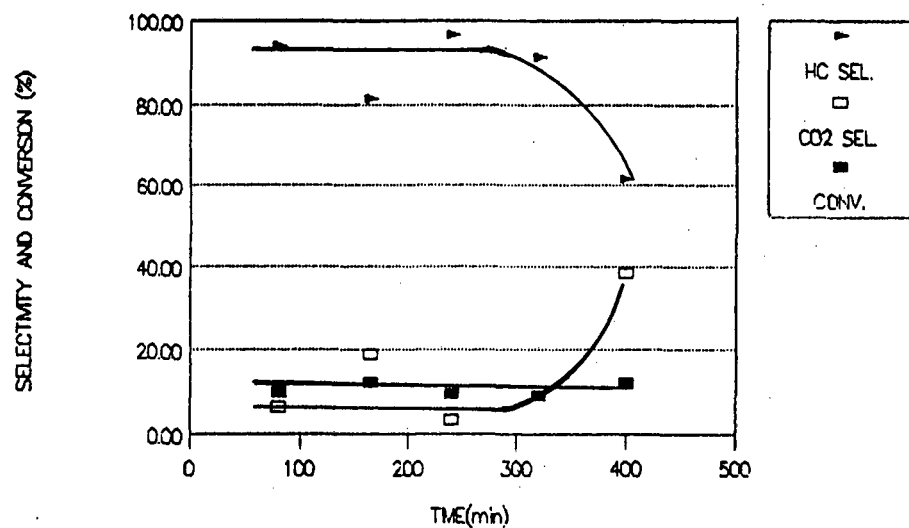
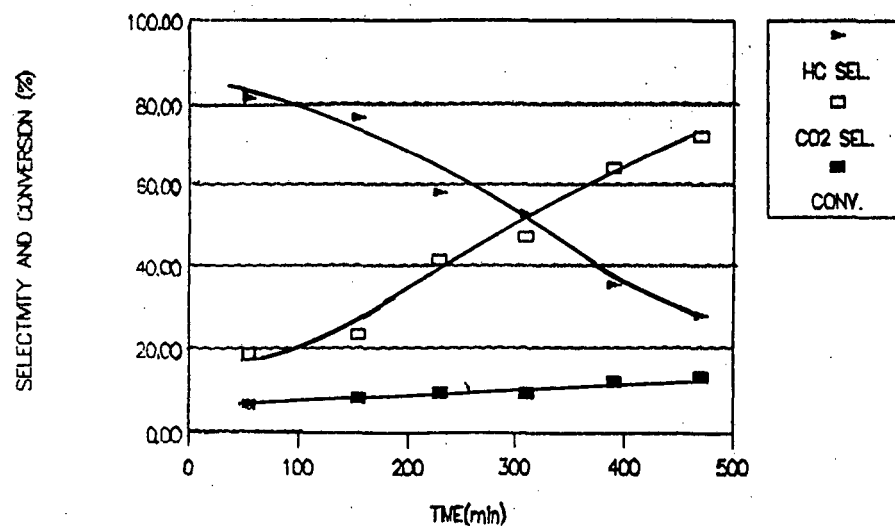
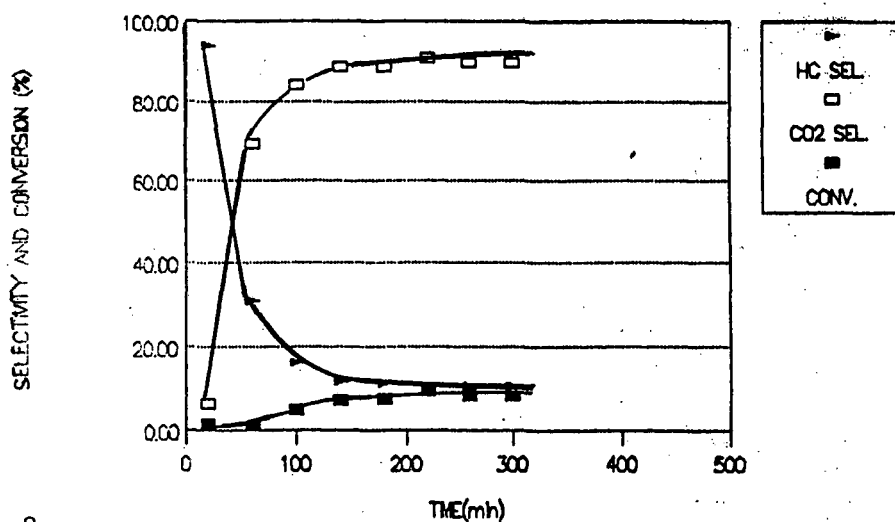
CH₄ COUPLING ON Ca₃NiK_{0.1}Sel. of HC and CO₂, conversionCH₄ COUPLING ON Ca₃CoK_{0.1}Sel. of HC and CO₂, conversionCH₄ COUPLING ON Ca₃FeK_{0.1}Sel. of HC and CO₂, conversion

Figure 8

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