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Fundamental Studies of the Mechanism of Catalytic Reactions with Catalysts Effective in the Gasification of Carbon Solids and the Oxidative Coupling of Methane. Quarterly Report, April 1, 1993 - June 30, 1993

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Author

Heinemann, H.

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QUARTERLY REPORT

April 1, 1993 - June 30, 1993

**FUNDAMENTAL STUDIES OF THE
MECHANISM OF CATALYTIC REACTIONS
WITH CATALYSTS EFFECTIVE IN THE
GASIFICATION OF CARBON SOLIDS AND THE
OXIDATIVE COUPLING OF METHANE**

Principal Investigators: Heinz Heinemann
Gabor A. Somorjai
Dale L. Perry

Center for Advanced Materials
Materials Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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I. Task Description for FY 1993

Task 1: Work on catalytic steam gasification with chars and coals will be extended from atmospheric to elevated pressures using the newly built pressure unit. The novel finding that coking of petroleum in the presence of small amounts of caustic greatly improves the gasification rates and characteristics of the coke will be extended to chars. The chars will be prepared by charring coals in the presence of minor amounts of caustic and the resulting chars will be steam gasified in the absence and presence of catalysts.

Task 2: In the oxidative coupling of methane over ternary catalysts, a large number of factors remain poorly understood and must be investigated to improve results and move them into the commercially interesting area. Emphasis will be placed on low temperature coupling and on the oxidative production of syngas from methane at low temperature. Work on the CRADA between LBL and Orion ACT will continue and will be expanded to include methane coupling to higher hydrocarbons in a membrane reactor. Isotope studies will be undertaken to better understand the nature of the active catalyst sites.

Task 3: Experimental work will continue on the synthesis of the mixed catalyst, and they will be characterized by a number of techniques, including elemental analyses, x-ray diffraction, and surface area determination. Scanning electron microscopy will be used to monitor the variations of the surface morphology as a function of the preparative route. X-ray photoelectron, Auger, Raman and infrared spectroscopy will be used to study chemical and bonding aspects of the catalysts.

II. Highlights

a) Catalytic Steam Gasification of Coals and Cokes

- A potential simplification of the catalytic steam gasification was found. Rather than charring coal or coke in the presence of caustic, equal or better results can be obtained by continuously introducing a small amount of NaOH with the steam as a 1% or less aqueous solution of NaOH.
- Using the three component K-Ca-Co oxide catalysts, it was shown that gasification rates improve somewhat with increasing cobalt content.
- Gasification rates for the K-Ca-Co oxide catalyst improve with increasing temperature, but appear to level out above 640°C.

- The activation energy for steam gasification of Ill #6 char over K-Ca-Co oxide catalyst is about 34 Kcal/mol.

b) Oxidative Methane Coupling

- In the membrane reactor difficulties have been encountered in establishing a good seal between the membrane and the reactor and with sintering of the membrane. These problems were overcome by substituting calcium for strontium in the perovskite membrane and by making thicker membranes.
- Testing of the oxidative coupling of methane in the membrane reactor are in progress, but results are too incomplete for interpretation at this time.
- Partial oxidation of methane to syngas over Co/MgO catalysts was further investigated. This includes: effect of Co-loading on catalyst activity; influence of contact time on the reaction of methane with oxygen; and partial pressure effect of methane on the reaction of methane with oxygen. It was found that catalysts with very low Co-loading; e.g., Co/MgO(A) (Co/Mg: 3/100) are not able to facilitate the reaction of methane with oxygen to produce syngas. In terms of catalyst performance for the reaction of methane with oxygen, there seems to be no difference between Co/MgO(B) (Co/Mg:3/10) and Co/MgO(C) (Co/Mg:3/1). High dilution ratio of the reaction mixture leads to lower conversion of methane and lower selectivities to carbon monoxide and hydrogen. It appears that a contact time of ~2ms is optimal. Shorter contact time results in lower conversion of methane and much lower selectivity to hydrogen and longer contact time leads to somewhat higher selectivity to hydrogen but much lower selectivity to carbon monoxide.

c) Synthesis and Characterization of Catalysts

- Thin layers comprised of calcium, nickel, and potassium oxide were made, and x-ray photoelectron spectroscopic studies were conducted in an attempt to gain a better understanding of the nature of the potassium oxide in the quaternary metal oxide catalyst system. In preliminary results, core level x-ray photoelectron lines were studied for the principal metals in the layers, along with the oxygen 1s lines. In the initially prepared

samples, all three metals and oxygen were readily observed in the spectra with binding energies that are in agreement with the normal oxidation states of the metal ions. Upon light sputtering, however, the nickel and calcium lines were still relatively intense, while the main potassium line had disappeared. There are only two possible explanations for this observation. First, the potassium was either principally or totally on the surface rather than in the lattice, and it was removed by the sputtering process. Alternately, the amount of potassium that was removed left only enough potassium in the lattice (or on the surface) such that it was not discernable from the background noise in the spectral region for potassium. Either explanation is quite plausible, since the potassium is originally present in only small, fractional amounts relative to the calcium and nickel. This work is being continued in light of these quite interesting results.

- Magnetochemical research continued on the Ca/Ni/K/O system, and a manuscript is being prepared that describes this work. Also, a paper *Applications of Magnetochemistry to the Characterization of Calcium-Nickel-Potassium Oxide Catalysts* was given at the 205th National Meeting of the American Chemical Society in Denver, Colorado. Patent applications are being prepared covering other work on this project.

III. Progress of Studies

a) Catalytic Steam Gasification of Coals, Chars and Cokes

The last quarterly report (LBL-33769) summarized results obtained with ternary catalysts; e.g., K-Ca-Ni oxide and K-Ca-Co oxide. It was also shown that chars prepared in the presence of NaOH were more easily gasified than the base char, even if the chars were washed to remove all residual free NaOH.

During the present report quarter, three variables were investigated:

- (i) The effect of varying the atomic ratio of different catalyst components (alkali vs. transition metal);
- (ii) The effect of steam partial pressure and of temperature on the reaction;
- (iii) Determination of activation energy of the reaction over K-Ca-Co oxide.

It was also found that if the water (steam) used for gasification contains a small amount of NaOH, gasification rates are greatly improved.

Figure 1 shows that the gasification rate improves with increasing Co content of the catalyst, though the differences between different Co contents are relatively small. A very similar effect was observed for different concentrations of Fe³⁺ in K-Ca-Fe oxide catalysts.

Figure 2 presents conversion vs. time plots for gasification of an Ill #6 char (which had been charred in the presence of 0.5% caustic) over a K-Ca-Co oxide catalyst at four temperatures. As expected the gasification rate increases with temperature, although there is little difference between our standard 640°C and 680°C.

Figure 3 investigates the effect of partial pressure of water on the conversion using an Ill #6 char (prepared in the presence of 0.5% caustic) and a K-Ca-Co oxide catalyst at 640°C. There is an improvement in rate with increasing water partial pressure.

Effect of Co atomic ratio in K-Ca-Co oxide catalysts on gasification of Ill#6 char

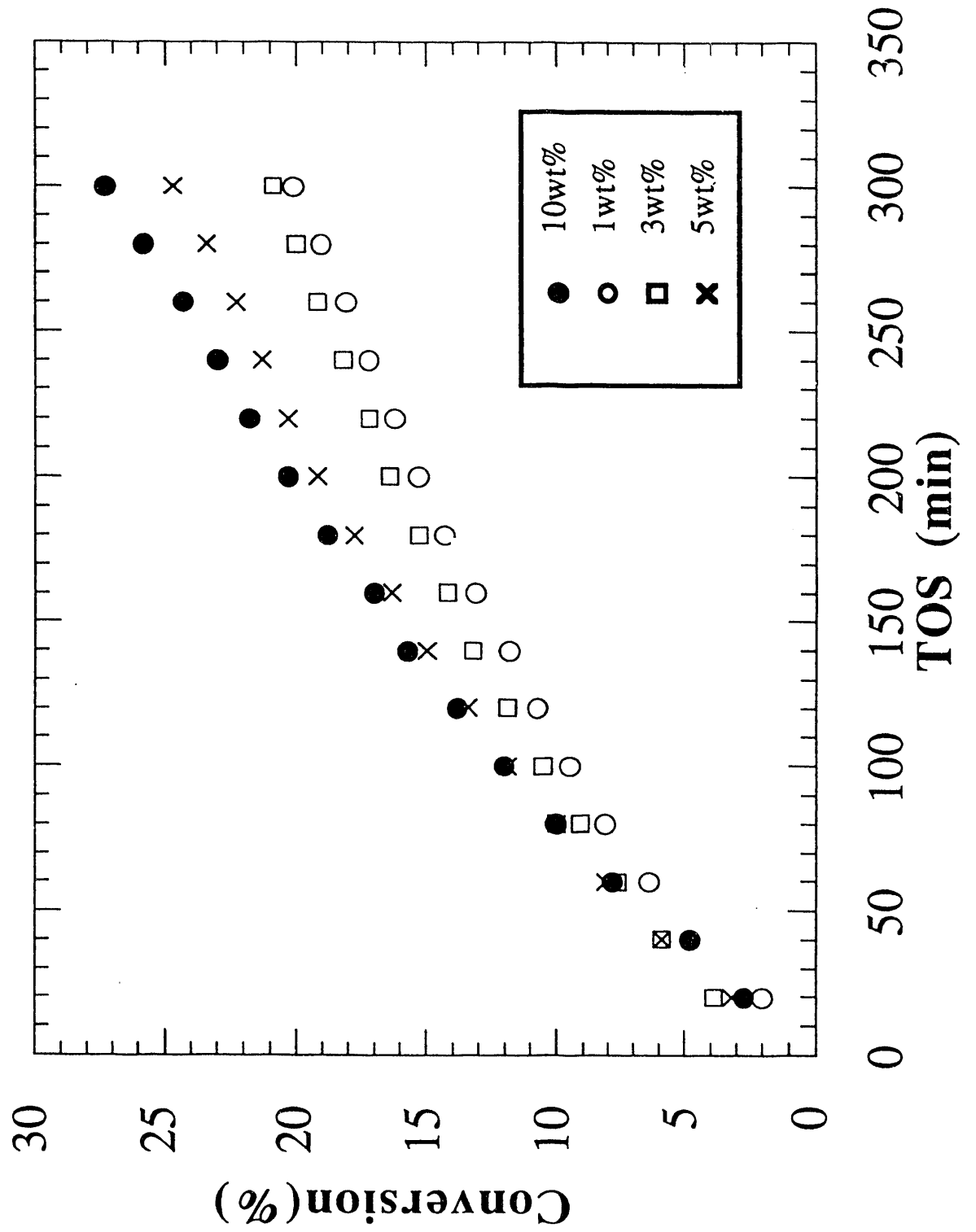


Figure 1

Effect of gasification temperature of Ill #6 char (charred with 0.5% NaOH) using a K-Ca-Co oxide catalyst.

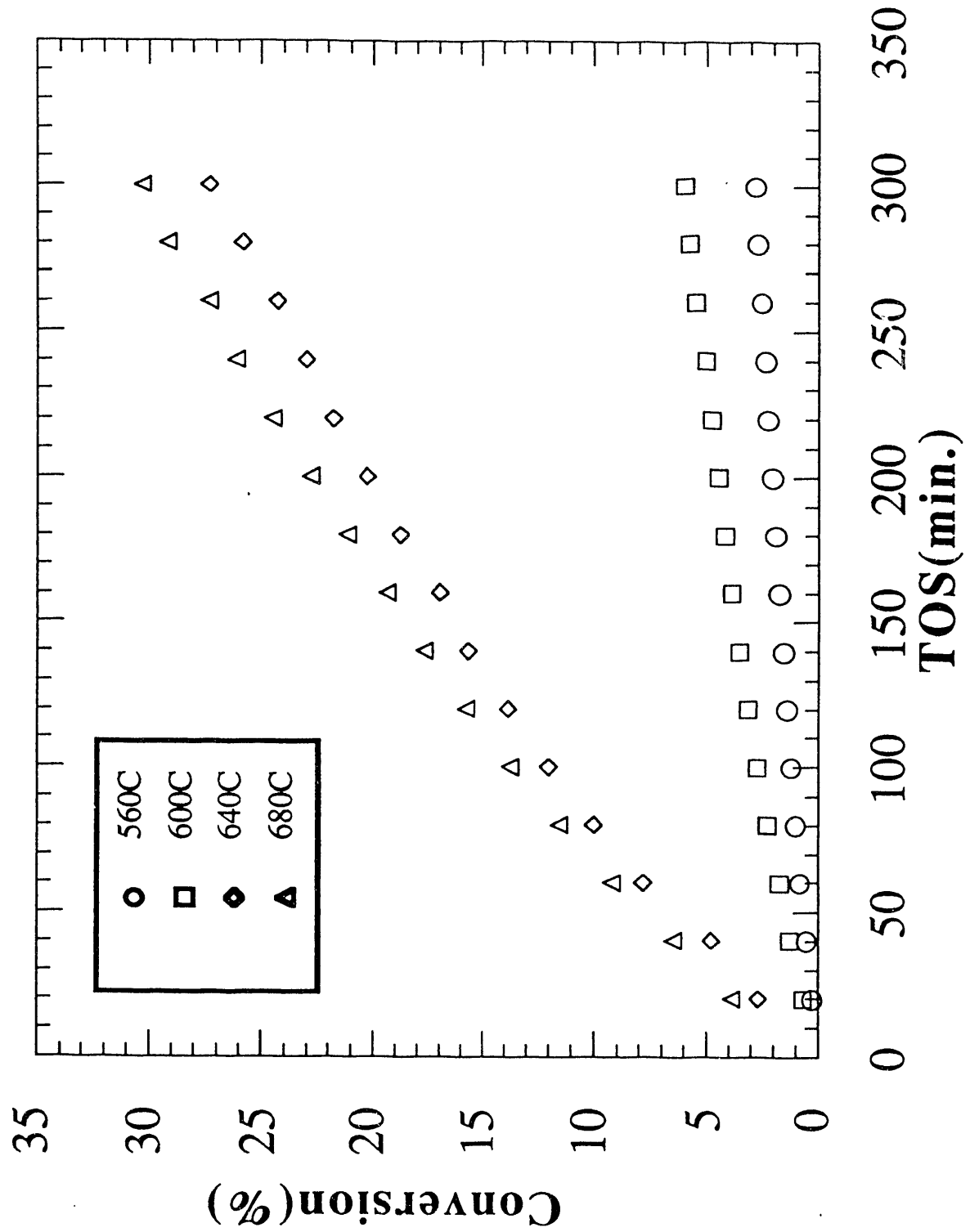


Figure 2

Effect of water partial pressure on gasification of I11 #6 char using a K-Ca-Co oxide catalyst at 640°C

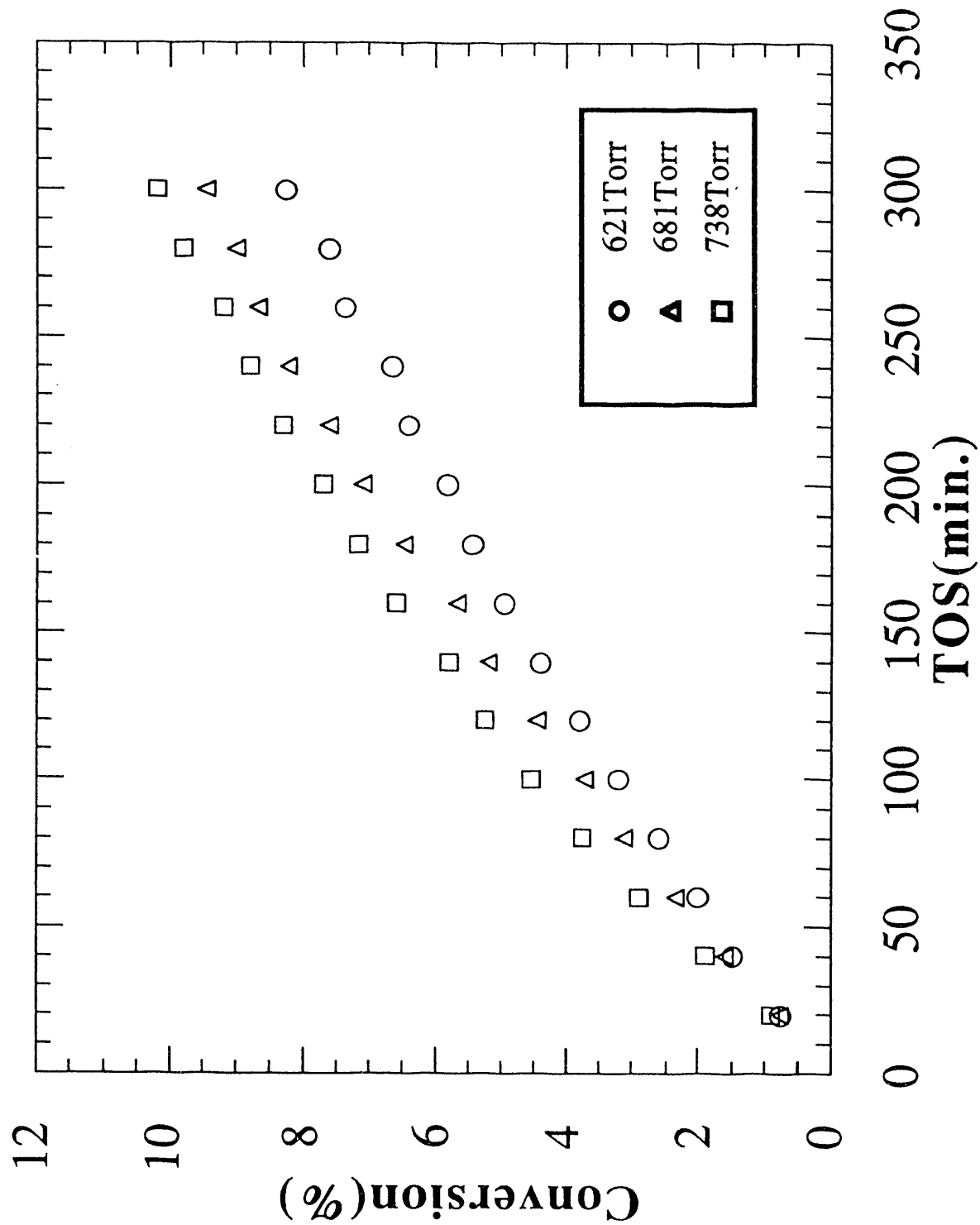


Figure 3

The apparent activation energy of steam gasification of Ill #6 char (prepared in the presence of 0.5% caustic) over K-Ca-Co oxide catalysts is given in Table 1.

Table 1: Apparent Activation Energy of Steam Gasification Over K-Ca-Co Catalyst

Reaction Time (min.)	Activation Energy (Kcal/mol)
20	36
100	34
200	33
300	33

The rate expression used for determining the activation energy is

$$R_c = K_f [P^a(\text{carbon}) P^b(\text{H}_2\text{O})] \quad (1)$$

where R_c is reaction rate, K_f is rate constant, $P(\text{carbon})$ is partial pressure of carbon, $P(\text{H}_2\text{O})$ is water partial pressure, and a, b is reaction order respectively.

Assuming carbon concentration is constant, the expression becomes as follows:

$$R_c = K_f' P^b(\text{H}_2\text{O}) \quad (2)$$

In the case of constant water partial pressure, the equation is simplified as follows:

$$R_c = K_f'' \quad (3)$$

By the Arrhenius law:

$$K_f'' = K_o \exp -E/RT \quad (4)$$

$$R_c = K_o \exp -E/RT \quad (5)$$

$$\ln R_c = \ln K_o - E/RT \quad (6)$$

The Arrhenius plot used in the calculation is shown in Figure 4.

It has recently been found that instead of charring the coal in the presence of caustic, it is advantageous to gasify the raw char with steam containing some NaOH (1% NaOH aqueous solution). The improvement is shown in Figure 5. A similar

Arrhenius plot for K-Ca-Co/III#6

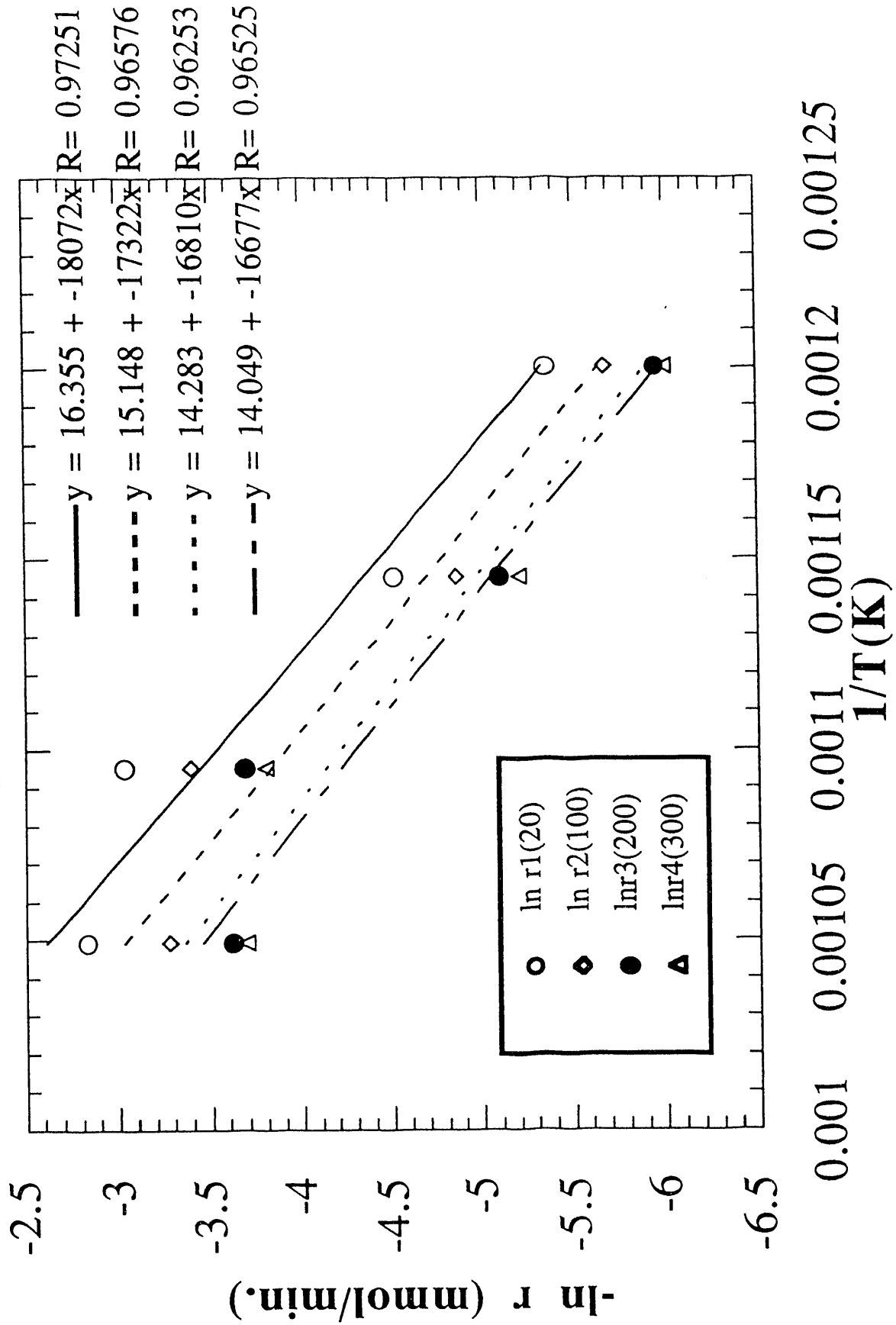


Figure 4

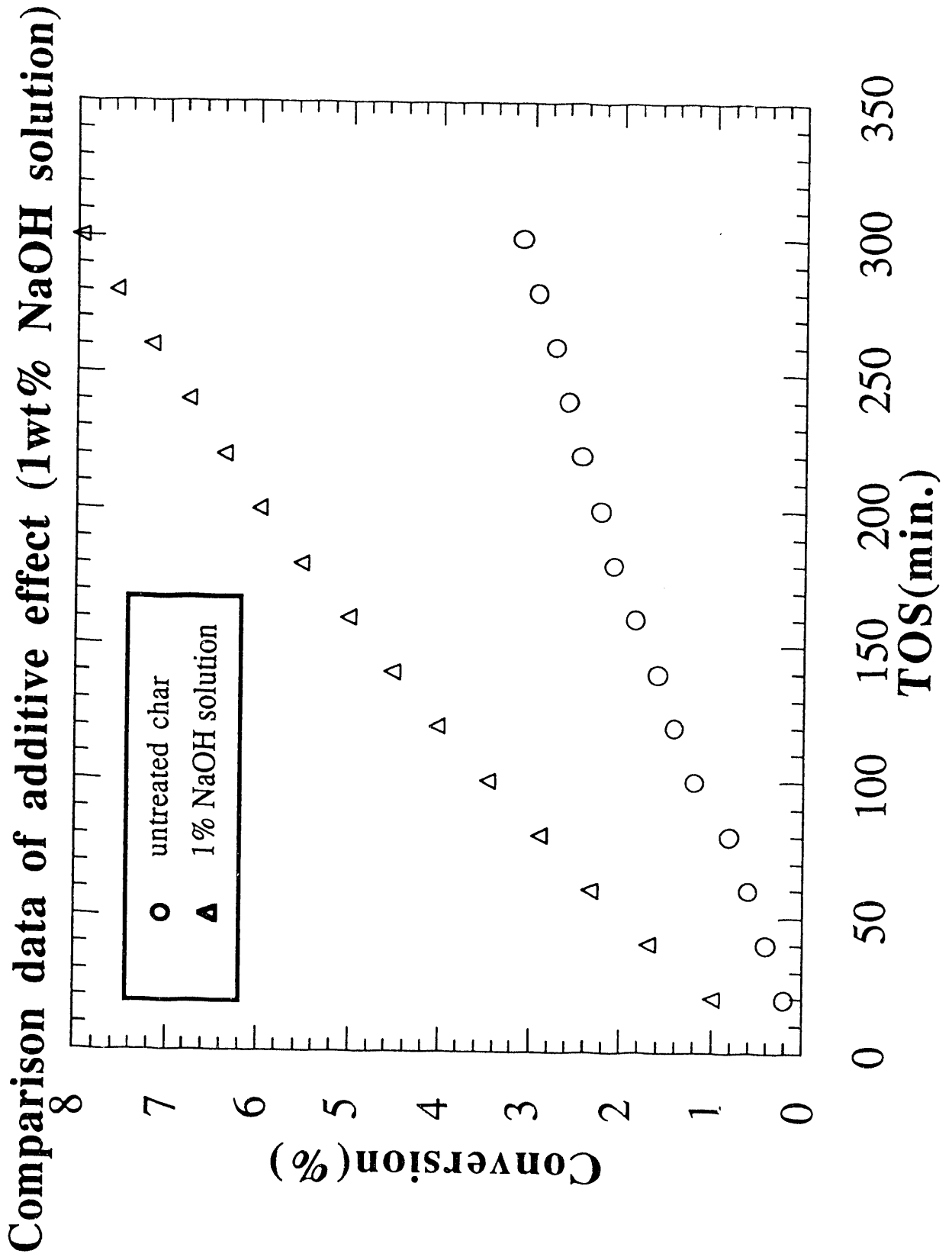


Figure 5

Comparison data of additive effect (1wt% NaOH solution)

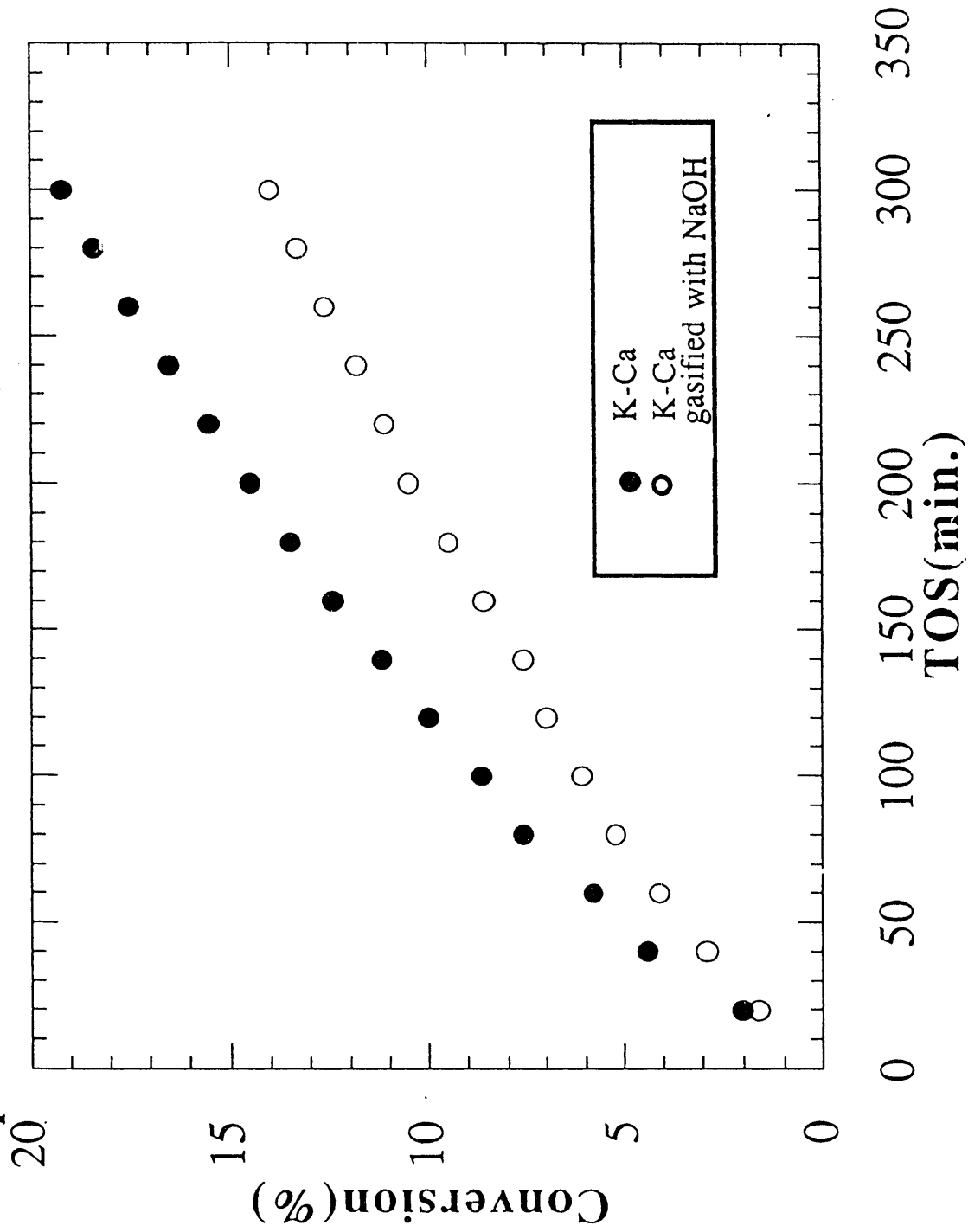


Figure 6

effect is shown when the raw char is impregnated with K-Ca oxide catalyst and then gasified with caustic containing steam (Figure 6). This finding potentially simplifies the catalytic steam gasification of coals and chars and will be further investigated.

b) *Oxidative Methane Coupling and Partial Oxidation of Methane*

Membrane Reactor

Design of a reactor and preparation of a membrane have been described in previous reports (LBL-33241 and 33769). Difficulties were encountered in obtaining seals between the reactor and the membrane. It was found necessary to produce thicker membranes. Thick membranes have been prepared by decomposition of SrCO_3 , ZrO_2 , and Y_2O_3 powders at 1100°C , forming the $\text{SrZr}_{0.2}\text{Y}_{0.1}\text{O}_{2.95}$ perovskite powder, which was confirmed by X-ray diffraction. The powder was then pressed and sintered in two stages at the high temperature facility: first at 1300°C to make a disk preform, then at 1600°C overnight. The disk appeared to be fine when removed from the furnace, but upon standing in air to cool, the surface expanded and cracked. Apparently, the sintering did not eliminate all the microporosity, allowing reaction with the air upon cooling. These problems were not observed when Ca was substituted for Sr. Membranes made with $\text{CaZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$, which is also a proton conductor, were more stable and have been installed into the reactor. Densification of the $\text{CaZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ perovskite membrane preform for ~16h at 1650°C led to noticeable shrinkage along with the introduction of some curvature, indicating that densification was not completely uniform across the thickness of the membrane (with the top shrinking slightly more than the bottom). The resultant membrane was ~34 mm across and 2 mm thick. The average membrane density is over 80% of the theoretical density, with the density near the top surface being much closer to theoretical. The average density indicates incomplete sintering, but any channels that might span the entire thickness of the membrane will be small (<1 μm in diameter), few (covering <1% of the surface), and tortuous. These channels should be unable to support gas diffusion across the membrane as they would be pinched off near the dense surface.

The membrane was cut to 25 mm in diameter and mounted with a zirconia-based ceramic paste into the reactor unit. Test data are too incomplete at report time to be calculated in this report.

Methane Partial Oxidation

Our previous results showed that partial oxidation of methane to syngas occurs on Co/MgO catalysts of high cobalt-loading at high temperatures. To initiate the reaction of methane with oxygen, a temperature of not higher than 500°C is sufficient. Due to the exothermicity of the reaction, the temperature of the catalyst under typical reaction conditions was around 1200°C although the temperature recorded by a thermocouple positioned on top of the catalyst bed was 600-700°C. The catalyst was glowing. The necessity of high reactant gas space velocity for achieving high selectivity to carbon monoxide and hydrogen over Co/MgO catalysts is probably more related to generation of a sufficient amount of heat to keep up with the heat dissipation of the reactor to maintain very high catalyst bed temperature (very close to adiabatic operation) at which non-catalytic partial oxidation of methane, steam reforming of methane, and CO₂-reforming of methane to form carbon monoxide and hydrogen can occur than to a possible kinetic effect caused by it. To address this problem, we experimented with varying contact time and changing diluent to reactants ratio, and with altering the pre-treatment conditions.

Tables 2 and 3 give results obtained on Co/MgO catalysts, CoO oxide, and MgO oxide at different temperatures. Co/MgO(A), CoO, and MgO did not show any activity or showed very low activity at 500°C. In contrast, both Co/MgO(B) and Co/MgO(C) catalysts showed very high activity for the reaction of methane with oxygen to produce syngas. At temperatures $\geq 600^\circ\text{C}$, CoO and MgO showed slight activity for complete oxidation of methane to form carbon dioxide and water. Co/MgO(A) showed significant activity at 680°C. Carbon monoxide was the major product. The selectivity to carbon monoxide is very close to that of Co/MgO(B) or Co/MgO(C) but the selectivity to hydrogen is much lower than for Co/MgO(B) or (C).

Table 4 summarizes the effect of pre-treatment on the catalyst activity. Catalysts reduced by hydrogen at 500°C are able to facilitate the reaction of methane with oxygen to produce syngas at temperature $\geq 400^\circ\text{C}$. However, catalysts treated in oxygen at 500°C before being reduced by hydrogen do not show activity at 512°C.

The effects of contact time on conversion and product selectivity are shown in Figure 7. It shows that a contact time of ~2ms is optimal because although longer

Table 2 Comparison of Activity of Different Co-containing Catalysts a

Catalyst ^b	Starting Temp, °C	Conversion %		Selectivity %		
		CH ₄	O ₂	H ₂	CO	CO ₂
—	500	0	0	—	—	—
CoO	503	<0.1	0.4	0	0	100
MgO	501	0	0	—	—	—
Co/MgO (A)	504	0	0	—	—	—
Co/MgO (B)	502	60	100	92	89	11
Co/MgO (C)	501	73	100	92	91	9

a, catalyst: 0.026 g; CH₄: 125 cm³·min⁻¹; O₂: 62.5 cm³·min⁻¹; N₂: 10 cm³·min⁻¹;

b, Co/MgO (A): Co: 4.2wt%; Co/MgO (B): Co: 28.7wt%; Co/MgO(C): Co: 66.7wt%;

Table 3. Comparison of Activity of Different Co-containing Catalysts ^a

Catalyst ^b	Starting Temp./°C	Conversion %		Selectivity %		
		CH ₄	O ₂	H ₂	CO	CO ₂
—	810	1.2	5	72	90	10
CoO	580	0.4	2	0	0	100
MgO	720	0.7	3	0	0	100
Co/MgO (A)	780	10.0	40	25	78	22

a, catalyst: 0.026 g; CH₄: 125 cm³·min⁻¹; O₂: 62.5 cm³·min⁻¹; N₂: 10 cm³·min⁻¹;

b, Co/MgO (A): Co: 4.2wt. %;

Table 4 Effect of Catalyst Pre-treatment on the Reaction of Methane with Oxygen over Co/MgO(B) ^a

Pre-treatment ^{b,c}	Temperature/°C	Reaction	Major Products
H ₂ /500°C	500	Yes	H ₂ , CO, CO ₂ , H ₂ O
H ₂ /500°C	395	Yes	H ₂ , CO, CO ₂ , H ₂ O
O ₂ /500°C	396	No	—
O ₂ /500°C; H ₂ /400°C	398	No	—
O ₂ /500°C; H ₂ /400°C	512	No	—
O ₂ /500°C; H ₂ /500°C	498	No	—

a, Co/MgO: 0.026g; CH₄: 125 cm³·min⁻¹; O₂: 62.5 cm³·min⁻¹; N₂: 10 cm³·min⁻¹;

b, H₂: mixture of hydrogen and helium containing 20% hydrogen (100 cm³·min⁻¹);

c, O₂: 100% oxygen: 20 cm³·min⁻¹;

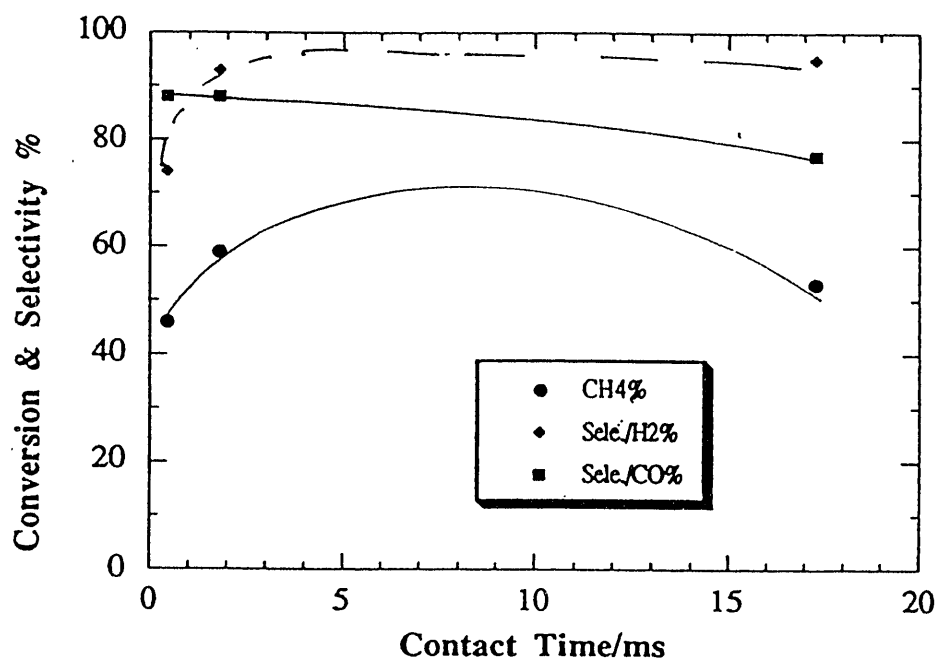


Fig. 7 Effect of contact time on the reaction of methane with oxygen over Co/MgO(B) catalyst at $\sim 700^{\circ}\text{C}$: CH_4 : $125\text{ cm}^3\cdot\text{min}^{-1}$; O_2 : $62.5\text{ cm}^3\cdot\text{min}^{-1}$; N_2 : $10\text{ cm}^3\cdot\text{min}^{-1}$.

contact time leads to somewhat higher selectivity to hydrogen, it is accompanied by decrease in selectivity to carbon monoxide, and shorter contact time results in lower selectivity to hydrogen.

One preliminary experiment was conducted with Dy_2O_3 for the partial oxidation of methane. This is because we had previously found that this catalyst was able to facilitate the oxidative coupling of methane at very high gas space velocity ($CH_4:90\text{ cm}^3\cdot\text{min}^{-1}$; $O_2:30\text{ cm}^3\cdot\text{min}^{-1}\cdot\text{g}^{-1}$) at relatively low temperatures ($\geq 350^\circ\text{C}$). Under the conditions used for Co/MgO catalysts, Dy_2O_3 showed similar behavior for the partial oxidation of methane to synthesis gas. Further experimentation is needed to draw conclusions for Dy_2O_3 .

c) *Synthesis and Characterization of Catalysts*

Initial studies were performed using x-ray diffraction techniques to get an understanding of the electronic nature of cobalt in mixed cobalt/magnesium/oxide catalysts. Upon preparing the catalysts and using them in several catalytic cycles, two main phases of magnesium and cobalt were unequivocally detected. A very clean, strong powder pattern was observed for Co_3O_4 in all the samples, while only MgO was detected as the phase for the magnesium oxide component. These are the only two phases for which there was any evidence. Thus, the cobalt exists electronically as both cobalt(II) and cobalt(III).

These syntheses are going to be pursued using dopant potassium in addition to the cobalt and magnesium, with the studies of their characterization being pursued using magnetochemistry and, additionally, x-ray diffraction, Fourier transform infrared, and x-ray photoelectron spectroscopy.

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