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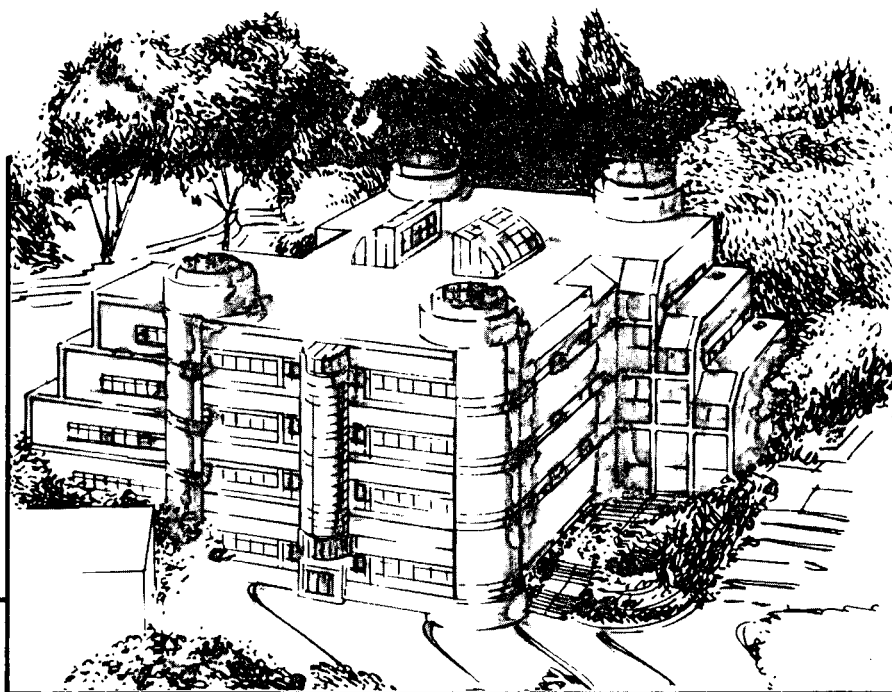
Fundamental Studies of Catalytic Gasification

Quarterly Report

April 1–June 30, 1991

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June 1991



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QUARTERLY REPORT

April 1, 1991 - June 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

Work during this quarter was largely concentrated on oxidative methane coupling. A paper on this subject was presented at the 12th North American meeting of the Catalysis Society and a publication, which is attached in the Appendix, has been accepted by a refereed journal. Some of the new work on catalyst preparation and testing is omitted from this report since it is the subject of potential patent applications.

Negotiations with several potential industrial collaborators have continued during the quarter. At the end of June, 1991, a tentative agreement was reached with ACT Orion USA in Wilmington, DE. The company will provide some support for work at LBL during October 1, 1991-September 30, 1993, will also undertake research in their laboratory in close coordination with LBL and if the research continues successfully, will undertake scale-up of both catalyst manufacture and process design and operation.

III. Highlights

a) Steam Gasification of Petroleum Cokes

- A high metals petroleum coke, which could not be steam gasified at our standard conditions in the absence of a catalyst gasified well in the presence of a K-CaO_x catalyst.
- It was demonstrated that method and conditions of the coking procedure can greatly influence the gasification rate. Coking in the presence of small amounts of caustic resulted in better gasification, both in the presence and absence of catalysts.

b) Oxidative Methane Coupling

- Free energies were calculated for conversion of methane and oxygen to ethane, ethylene and water and showed the reaction to be slightly exothermic.
- The activation energies for production of C₂ hydrocarbons from methane and oxygen and for conversion of methane to syngas and CO₂ were calculated.
- Carbon balances around the reactor were found to be 100% ± 2%.
- Experiments in an empty reactor and in a reactor charged with quartz chips gave conversions of methane to CO₂ of 1-2%. This indicates that the CO₂ found with C₂+ hydrocarbons in runs over a catalyst is due to purely thermal reaction.
- Runs of 6 and 19 hours duration gave 92-93% selectivity to higher hydrocarbons at 10% conversion, with the 7-8% conversion to CO₂ being thermal conversion. The catalytic selectivity, therefore, was 100%.

- A series of catalysts was prepared comprising two of the normal three catalyst components. Only the ternary catalyst gave high selectivity.
- A catalyst comprising cobalt instead of nickel ($\text{Ca}_3\text{Co}_1\text{K}_{0.1}$) gave much poorer results than the nickel containing catalyst.

IV. Progress of Studies

a) Catalytic Steam Gasification of Petroleum Cokes

Gasification of a Maya coke was undertaken in the presence and absence of a K-CaO_x catalyst. The same petroleum coke was alternatively treated at 450°C with water under pressure or with dilute caustic under pressure prior to gasification. Results are shown in Figs 1 and 2. The Maya coke could not be gasified at our standard conditions in the absence of catalyst but gasified reasonable well in the presence of 1% catalyst (Fig. 1). Pretreatment of the coke with water or with caustic improved gasifications (Fig. 2). Even in the absence of catalyst, the caustic treated coke was superior to the Maya coke with catalyst. Combining caustic pretreatment with catalytic gasification resulted in very superior gasification rates.

b) Oxidative Methane Coupling

Free energies were calculated for the 120-1200°C temperature range for 5 reactions which may occur during oxidative coupling.

- 1) $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$
- 2) $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$
- 3) $\text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$
- 4) $\text{CH}_4 + 1/2\text{O}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O}$
- 5) $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$

These are shown in Fig. 3. As is obvious, combustion (1) is very exothermic, steam reforming (2) and dehydrogenation (5) are endothermic and methane coupling to ethane (4) or ethylene (3) are only slightly exothermic.

It was also determined that the activation energy for (3 and 4) is 83 KJol/mole, while that for (2) is 263 KJol/mole.

A careful carbon balance was performed to insure that analytical results would not be influenced by a potential absorption of CO₂ produced by the catalyst with formation of calcium carbonate. Carbon input (as methane) and carbon output (as methane, higher hydrocarbons and CO_x) were metered and analyzed. Table 1 shows the carbon balance for two runs, one at high selectivity and the other at relatively poor selectivity. A blank run with an empty reactor at the same conditions gave .8 to 1.0% conversion to CO₂ (Table 2). This corresponds exactly to the CO₂ selectivities obtained with catalyst in the reactor (8-10% at 10% conversion, Table 1), and indicates that CO₂ was formed thermally and none was absorbed on the catalyst. Excellent balances were obtained. An oxygen balance is difficult to obtain because water formed during oxidative coupling is a small fraction of the water used as steam. It is interesting to note that when the reactor was charged with quartz chips (no catalyst) the CO₂ production almost doubled.)

CaO, CaK_{0.1}O_x, Ca₃NiO_x, NiK_{0.1}O_x and Ca₃NiK_{0.1}O_x catalysts were tested at the same reaction conditions (600°C, CH₄:O₂:H₂) = 3:1:6.5). The results obtained are shown in Table 3. CaO alone produced mainly CO₂ and CO (82.0-77.2% and 7.0-11.0%, resp.); only 9.0-11.4% selectivity for hydrocarbons was found at a conversion of 4.8-2.3%. Introducing a small amount of potassium onto CaO, the hydrocarbon selectivity increased up to 80% at a conversion of 4.7-4.6%. The presence of potassium suppressed CO₂ and CO formation. This is also reflected in the results obtained on Ca₃NiO_x (without potassium) where the starting value of hydrocarbon selectivity (43.7%) decreased considerably with time on stream, while CO₂ formation became dominant. On NiK_{0.1}O_x a relatively high conversion (16.9-15.6%) was observed; the main reaction product was CO₂ (i.e., total oxidation was dominant). The most active and selective catalyst proved to be Ca₃NiK_{0.1}O_x.

It is interesting to note that in the presence of potassium (see CaK_{0.1}O_x) a small amount of CO was observed. It can be inferred that steam reforming of CH₄ occurs on CaK_{0.1}O_x. The absence of CO among the reaction products in the presence of Ni may indicate the ability of Ni to oxidize CO to CO₂ in the presence of oxygen.

Table 1 Carbon balance for two runs at different conversion and selectivity values Ca₃ Ni₁ K_{0.1} Catalyst C output/C input					
Catalyst	Time min	Conversion %	Hydrocarbon Selectivity, %	CO _x Sel %	Carbon Balance
A	60	10	93	7	99.8
A	120	10	92	8	100.1
B	50	4	80.3	20	101.8
B	130	5	48.3	52	104.7
B	165	3	83.3	17	101.3
B	205	4	56.9	43	101.3
B	245	3	78.9	21	98.6

Table 2 EMPTY REACTOR 600°C; CH₄:O₂:H₂O = 3:1:6.5 moles			
Period	CH ₄ Conv. %	CO ₂ yield. %	C ₂ -C ₄ yield. %
1	1.0	.9	.12
2	.9	.8	.12
3	.8	.7	.11
4	.8	.7	.11

Table 3 Characteristic Data of CH₄ Coupling On Different Catalysts 600°C; CH₄:O₂:H₂O = 3:1:6.5; atm. press.					
Catalyst	Conversion	HC Sel.	CO ₂ Sel.	CO Sel.	CO _x Sel.
CaO	4.8-2.3%	9.0-11.4%	83.0-77.5%	7.0-11.0%	90.0-88.5%
CaK _{0.1}	4.7-4.6%	81.5-79.9%	16.6-17.5%	1.8-2.5%	18.5-20.0%
Ca ₃ Ni	3.1-6.7%	43.7-11.0%	56.2-88.9%	0	
NiK _{0.1}	16.9-15.6%	2.1-2.3%	97.8-97.6%	0	
Ca ₃ NiK _{0.1}	9.9-9.0%	93.7-91.1%	6.3-8.9%	0	

Table 4 Methane oxidative coupling run. Conversion and selectivities Ca₄ Ni₁ K_{0.1} Catalyst 600°C; CH₄:O₂:H₂O = 3:1:6; atm. pressure			
Time min	CH ₄ Conv. %	Hyd. Sel. %	CO _x Sel. %
95	10.6	91	9
153	9.3	92	8
212	9.2	92	7
271	10.0	93	7
329	8.8	88	11
388	9.3	92	8

Table 5 Methane oxidative coupling run; product distribution Ca₄ Ni₁ K_{0.1} Catalyst 600°C; CH₄:O₂:H₂O = 3:1:6; atm. pressure						
Time min	C ₂ H ₄ sel %	C ₂ H ₆ sel %	C ₃ H ₆ sel %	C ₃ H ₈ sel %	C ₄ sel %	Par/Ol Ratio
95	42	40	3	4	2	.98
153	40	41	4	4	3	1.0
212	40	41	5	4	3	1.0
271	39	42	5	4	3	1.1
329	44	33	5	4	2	0.8
388	41	40	5	3	3	1.0

Table 4 presents results from a typical run at 600°C during 6.5 hours. Conversion was quite steady as was selectivity at ≈92%. It is important to point out that blank runs with an empty reactor at the same conditions gave .7-1.0% conversion of CH₄ to CO₂. This amount of CO₂ would correspond to 7-10% CO₂ selectivity at 10% conversion or about what is observed in runs with a catalyst.

Table 5 gives a product distribution of the same run as in Table 4. Again all selectivities were steady. Small amounts of C₃ and C₄ hydrocarbons were formed and the olefin/paraffin ratio was about 1.0. The longest run thus far made lasted about 19 hours. It showed only a small decline in activity and selectivity, probably due to a unit upset after 10 hrs.

A catalyst was prepared by the standard method that contained cobalt instead of nickel. The atomic proportions charged to the preparation were Ca:Co:K = 3:1:0.1. While initially active and selective similar to the nickel catalyst, the hydrocarbon selectivity started dropping from 82% after the first hour of operation to 20% after 10 hours and production of CO₂ increased correspondingly to 80%. This catalyst is therefore not a good catalyst for oxidative methane coupling.

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