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Fundamental Studies of Catalytic Gasification

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QUARTERLY REPORT

FUNDAMENTAL STUDIES OF CATALYTIC GASIFICATION

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University of California
Berkeley, CA 94720

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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 slow because of major changes and revisions in laboratory set-up and procedures before and during the visit of the Tiger Team in January and February. There also was a change of a post-doctoral fellow with the need for the new person to familiarize himself with background and procedures.

Following publication of the paper on methane coupling (which was in the appendix of the December 31 report) there has been considerable industrial interest in this work. At the present time there are three companies sufficiently interested in potential collaboration with LBL to have entered into negotiations toward an agreement to participate in the research and evaluate scale-up to commercial operation. A decision will have to be made in the near future concerning which partner to select.
III. Highlights

a) Catalytic Steam Gasification

- The summary report on catalytic gasification fundamentals using mono or binary oxide catalyst systems is near completion.
- Three additional petroleum cokes have been catalytically gasified and found to exhibit similar characteristics as those previously reported.
- Gasification of coke #1, which was the only coke tested to behave more like graphite than coal, at 100°C higher temperature in the presence of Ca-K-O catalyst resulted in a better rate of gasification initially, but also in loss of catalyst activity after about 70% conversion.

b) Oxidative Methane Coupling

- Calcium-nickel-potassium oxide catalysts were prepared from different precursors. Though the catalyst series derived from nitrates appeared to be better than others, the differences are small and seem less important than activation procedure and operating variables.
- Catalysts were activated and reactivated in either oxygen or oxygen and steam. Activation in steam alone gave poor results. At this time no definitive conclusion can be drawn on the relative advantages of oxygen or oxygen-steam activation.
- Much work was undertaken to obtain good carbon balances and to ensure exact proportioning of CH₄, O₂ and H₂O flows through the reactor. It appears that the methane/oxygen ratio can be reduced and space velocity increased without major effect on selectivity.
- Attempts to increase bed length at constant contact time by mixing catalyst with glass wool resulted in poorer performance, probably due to by-passing.
A Ca-K-oxide catalyst without nickel performed similarly to earlier runs with catalysts obtained from coal gasification, giving only up to 80% selectivity at 5% conversion.

IV. Progress of Studies

a) Catalytic Steam Gasification of Petroleum Cokes

The summary report on Catalytic Steam Gasification of Graphite, Chars and Coal over Potassium Oxide, Potassium-Nickel Oxide and Potassium-Calcium Oxide Catalysts is nearing completion and should be ready for submission by the end of the next quarter.

The work on catalytic gasification of petroleum cokes with different composition and metal contents was continued. Table 1 gives the composition of all the cokes that have thus far been evaluated. The analysis for cokes #8, 9 and 10 has not been previously shown. The procedure for gasifying these cokes was the same as previously described in the December report.

<table>
<thead>
<tr>
<th>Number</th>
<th>%C</th>
<th>%H</th>
<th>%O</th>
<th>%S</th>
<th>ppmNi</th>
<th>ppmV</th>
<th>ppmFe</th>
<th>ppm Total Metals</th>
</tr>
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<tr>
<td>1</td>
<td>87.6</td>
<td>3.55</td>
<td>2.39</td>
<td>2.55</td>
<td>707</td>
<td>1090</td>
<td>832</td>
<td>2629</td>
</tr>
<tr>
<td>2</td>
<td>86.1</td>
<td>3.61</td>
<td>1.48</td>
<td>6.12</td>
<td>422</td>
<td>1919</td>
<td>1166</td>
<td>3507</td>
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<tr>
<td>3</td>
<td>92.8</td>
<td>3.90</td>
<td>1.41</td>
<td>0.55</td>
<td>147</td>
<td>20</td>
<td>3844</td>
<td>4011</td>
</tr>
<tr>
<td>4</td>
<td>88.6</td>
<td>3.76</td>
<td>0.97</td>
<td>5.13</td>
<td>223</td>
<td>657</td>
<td>209</td>
<td>1089</td>
</tr>
<tr>
<td>5</td>
<td>87.7</td>
<td>3.18</td>
<td>1.07</td>
<td>5.62</td>
<td>334</td>
<td>809</td>
<td>536</td>
<td>1679</td>
</tr>
<tr>
<td>6</td>
<td>90.9</td>
<td>4.0</td>
<td>0.42</td>
<td>4.45</td>
<td>12</td>
<td>5</td>
<td>99</td>
<td>116</td>
</tr>
<tr>
<td>7</td>
<td>86.6</td>
<td>3.35</td>
<td>0.93</td>
<td>7.96</td>
<td>175</td>
<td>509</td>
<td>178</td>
<td>862</td>
</tr>
<tr>
<td>8</td>
<td>83.3</td>
<td>4.2</td>
<td>2.0</td>
<td>0.4</td>
<td>625</td>
<td>1283</td>
<td>530</td>
<td>2438</td>
</tr>
<tr>
<td>9</td>
<td>88.6</td>
<td>4.37</td>
<td>0.97</td>
<td>5.13</td>
<td>255</td>
<td>705</td>
<td>209</td>
<td>1169</td>
</tr>
<tr>
<td>10</td>
<td>87.8</td>
<td>4.24</td>
<td>1.12</td>
<td>5.51</td>
<td>310</td>
<td>755</td>
<td>101</td>
<td>1166</td>
</tr>
</tbody>
</table>
Figure 1 is a repeat of Fig. 1 in the December report with the data for three additional cokes (#4, 7 and 10) added. These three cokes fall well within the range of the majority of those previously evaluated and only the coke #1 remains different from all the others. Thus, it appears that most of the cokes regardless of composition behave similarly to subbituminous coal with the one exception of coke #1, which behaves more like graphite. This would suggest that during coking an attempt should be made to not coke to graphitizing of the residual coke.

Figure 2 is a reevaluation of coke #1 with calcium-potassium oxide catalysts at 100° higher gasification temperature. It indicates that at the higher temperature a rate improvement is obtained but also that there is a deactivation of catalytic activity over time resulting in lower overall gasification.

Figure 3 presents a comparison of a nickel-potassium-oxide catalyst with calcium-potassium-oxide catalyst at 600° and also shows the performance of the calcium-potassium-oxide catalyst at 675°. This is for catalyst #5. The nickel containing catalyst is initially slightly more active but rapidly deactivates probably due to the sulfur content of the coke. At 75° higher temperature the calcium-potassium oxide catalyst shows better rate than at the lower temperature.

b) Oxidative Methane Coupling

During the report period there have been numerous inquiries from industrial organizations expressing interest in high selectivity oxidative coupling. Three of these inquiries have progressed to the stage of contract discussions, involving potential research support at LBL by an industry, industry work on economic evaluation and process and pilot plant research and licensing arrangements under pending patent applications. It is expected that an agreement with one of these companies will be signed within the next few months.

Three major variables have been identified which affect the catalyst conversion, selectivity and stability. They are: (1) catalyst preparation and composition; (2) catalyst activation procedure; (3) operating variables.

(1) Catalyst Preparation. Catalysts have been prepared by three methods: (a) from a mixture of the three nitrates, drying, decomposing and calcining at 700°C (PS series); (b) from the oxides, drying and calcining at 700°C (DP series); (c) from a mixture of calcium and
nickel nitrates, drying, decomposing and calcining then adding KNO₃, drying decomposing and calcining (IW series).

Figure 4 shows two consecutive runs with a PS catalyst (atomic ratio Ca:Ni:K = 4:1:0.1) at standard conditions (600°C; CH₄:O₂:H₂O = 3:1:6). LHSV = 4mmol/hr giving about 90-94% hydrocarbon selectivity at 9-12% conversion. The catalyst was activated before the first run and between runs in oxygen at 700°C. While the stability was quite good, the voluntary termination of the runs after six hours did not permit any conclusion on cycle length.

A DP series catalyst of a different composition (Ca:Ni:K - 2:1:0.1) and preparation showed similar results (Fig. 5) over an extended period of time (20 hrs), somewhat distorted by a temporary feed flow instability. However, this catalyst was very sensitive to the pretreatment procedure. The run in Fig. 5 was after pretreatment in O₂ and H₂. After pretreatment with either O₂ or H₂O alone it had low or short lived selectivity after as little as one hour on stream.

A IW series catalyst was initially inactive in the first run, but after repeated oxygen treatment showed relatively good (84%) selectivity at low conversion (∼5%) for 25 hours (Fig. 6a) after which selectivity to hydrocarbons suddenly dropped with commensurate increase in COₓ selectivity. After regeneration in O₂ and H₂O good stability was obtained for about 23 hours (Fig. 6b) when the run was terminated.

The preliminary conclusions are that the PS and DP series of catalyst are better than the IW series, but that catalyst preparation is a less important factor than pretreatment and operating variables.

(2) Catalyst Activation. A large number of runs were performed in which various catalysts were activated either by oxygen or by oxygen plus steam pretreatment. Present results are confusing. It is clear that steam pretreatment alone does not result in an active methane coupling catalyst, but in a catalyst having steam reforming activity. In Fig. 7 the catalyst used was a relatively poor activity DP series catalyst which after oxygen activation showed 92% selectivity at 9% CH₄ conversion, but deactivated after about 150 minutes. When it was attempted to reanimate the catalyst with oxygen (Fig. 7, run 3) about 40% hydrocarbon and 60% COₓ selectivity were obtained at 9-10% conversion. The catalyst was then reactivated with an equimolecular mixture of steam and oxygen (Fig. 7, run 5) and exhibited ∼90% hydrocarbon selectivity for about 450 min. After repeated steam-oxygen
reactivation (Fig. 7 run 8 and Fig. 5) high selectivity was preserved for at least 1000 minutes. The temporary and reversible decline after 300 minutes was due to a feed flow instability.

A different catalyst of the PS series was as has been shown in Fig. 4 active after oxygen treatment (run 1) and again active and selective after oxygen regeneration.

(3) Operating Variables. There is a large number of operating variables such as temperature, input and output flows, ratio of flow components and space velocity. It has been shown before (December 1990 report) that 600°C is a critical temperature and that above it steam reforming rather than methane coupling becomes the dominant reaction. A great deal of work has been and is being done to assure the correctness of results and to avoid artifacts, such as absorption of CO₂ on the catalyst and errors in conversion and selectivity due to poor material balances. It is too early to present meaningful data at this time. Early indications are that the CH₄:O₂ ratio can be doubled without materially affecting conversion or selectivity and that higher space velocities are feasible.

(4) Other Work. Early attempts to increase catalyst surface area by depositing the catalyst on silica or alumina had resulted in reduced activity and selectivity. A more recent experiment to increase the catalyst bed by mixing the same amount of catalyst usually used with an equal volume of glass wool also resulted in a loss of conversion and selectivity as shown in Table 2.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion</th>
<th>Hydrocarbon Select. %</th>
<th>CO₂ Select %</th>
<th>Length of run hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsupported O₂ treated</td>
<td>9-11</td>
<td>91.96</td>
<td>9.3</td>
<td>5</td>
</tr>
<tr>
<td>Mixed with glass wool O₂ treated</td>
<td>7-8</td>
<td>61.80</td>
<td>38.19</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 2
Catalyst PE (Ca 3:Ni 1:K 0.1); 600°C; 4mmol CH₄/hr
CH₄:O₂:H₂O = 3:1:6 mole
To supplement earlier work which had shown that calcium-nickel-oxide catalysts without potassium gave high initial selectivity but had poor stability (September 30, 1990 report) a catalyst was prepared from calcium and potassium only (1:0.1 ratio) in the absence of nickel. Figure 8 shows that after oxygen pretreatment this catalyst gave 5-8% CH₄ conversion and hydrocarbon selectivities of 40 to 80% depending on the ratio of steam to methane. The highest selectivity (and lowest conversion) was obtained at a low steam/methane ratio and therefore at a low space velocity. This result confirms earlier work with CaK oxide catalyst in the presence of carbon.
Figure 1

COKES WITH CATALYST (KCa), STANDARD CONDITIONS
CONVERSION VS TIME

conversion (fraction)

time (min)
Figure 2

STEAM GASIFICATION OF COKE #1

CONVERSION

TIME (min)

--- no catalyst 600°

--- Ca-K-O 600°

+++ Ca-K-O 700°
Fig. 4

CH4 COUPLING ON CaNiK0.1(PS-725/RUN1)

REACTION PERFORMANCES VS. TIME

CH4 COUPLING ON CaNiK0.1(PS-725/RUN2)

REACTION PERFORMANCES VS. TIME

Figure 4
CH4 COUPLING ON Ca2NiK0.1(DP–6/2)RUN8
REACTION PERFORMANCES VS. TIME (H2O+O2)
Fig. 6a

CH4 COUPLING ON Ca2NiK0.1(IW700,0X)

PARAMS. OF REACTION VS. TIME

Fig. 6b

CH4 COUPLING ON Ca2NiK0.1(IW700,02+H2O)

PARAMS. OF REACTION VS. TIME
CH₄ COUPLING ON Ca₂NiK₀.₁(DP–6/2)RUN3
REACTION PERFORMANCES VS. TIME (O₂)

CH₄ COUPLING ON Ca₂NiK₀.₁(DP–6/2)RUN5  CH₄ COUPLING ON Ca₂NiK₀.₁(DP–6/2)RUN8
REACTION PERFORMANCES VS. TIME (H₂O+O₂)REACTION PERFORMANCES VS. TIME (H₂O+O₂)
CH₄ COUPLING ON CaK₀.₁(Oₓ.)

CONVERSION VS. TIME


HC AND COX SEL. VS. TIME

END

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