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QUARTERLY REPORT
January 1, 1988 - March 31, 1988

FUNDAMENTAL STUDIES OF CATALYTIC GASIFICATION

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I. Task Description for FY 1988

In the past this program has investigated the role of catalysts in relatively low temperature steam gasification. New mechanisms have been demonstrated and it has been shown that combinations of alkali hydroxide with transition metal oxides form compounds which act as the true catalyst to produce mostly hydrogen and carbon dioxide. This has further been confirmed by surface science studies and by transmission electron microscopy. At the lower temperatures (~800 K) used, hydrogen and $\text{CO}_2$ are the products formed, but the effect of temperature and of the exact composition of the NiO/KOH catalyst that has been studied in the greatest detail on the $\text{CO}_2$/CO ratio remains to be defined. Similarly, a clear definition of the advantages of different alkali-transition metal oxide compositions is required. It appears possible that with the right catalyst and conditions, either syn-gas or $\text{H}_2 + \text{CO}_2$ can be produced. Inexpensive transition metal oxide-alkali catalysts will be evaluated as will be the effect of mineral matter in chars and coke and the role of different partial pressures of $\text{H}_2$, CO and $\text{H}_2\text{S}$.

II. Introduction

Experimental work in the second quarter of fiscal 1988 was somewhat limited by an extensive reconstruction of experimental apparatus and a change in scientific personnel. While interesting data were obtained and are reported in this report, conclusions are still tentative and need to be further confirmed.

III. Highlights

- The experimental setup was changed to a vertical instead of a horizontal reactor and improvements were made in temperature control and pumping and metering equipment.
In experiments with both graphite and demineralized char it was found that mixtures of earth alkali with potassium as catalysts exhibit good gasification characteristics. K-Mg is the most active and only somewhat less active than K-Ni. K-Ca is less active than K-Mg. The alkali-earth alkali catalysts show less initial deactivation and greater stability than K-Ni. Alkali-earth alkali catalysts are, of course, cheaper than alkali-transition metal catalysts and will probably be more sulfur resistant.

The alkali-earth alkali mixtures can dissociate water at the operating temperatures (>800k) and there is evidence that a mechanism may prevail that involves carbon oxidation by the oxygen from water and simultaneous generation of hydrogen.

An additional factor in catalyst activity is the ability of the catalyst to wet and spread over the carbon surface. This is dependent on the melting point of the mixture which is lower for K-Mg and for K-Ni than for a Mg-Ni mixture.

A previously proposed reaction scheme is expanded and is supported by experimental work.

IV. Progress of Studies

A. Experimental

The experimental setup of the flow reactor has been changed. Fig. 1 is a diagram of the system. The Reactor is a 3.7 mm ID 316 stainless steel tube. Between 0.5 and 1.0 g of sample is deposited between two alumina wool plugs. Passing steam through the system in the
absence of a sample does not give any reaction. The reaction temperature can be adjusted to ±1°C of the desired value. Steam is produced by pumping water with a Harvard Compact Infusion pump, Model 975, through heated lines with an inlet temperature to the reactor of 180°C. At water flows of less than 0.1 cc/min total pressure in the reactor is 15 psig ±1 psig. A liquid rate of .06 cc/min was selected as a standard flow, equivalent to 270 cc/min of steam at 580°C. Steam leaving the reactor is condensed by volume expansion. Gas produced is measured and analyzed by gas chromatography and liquid water is measured to permit a mass balance.

A thermal detector with a column of 100/120 carbosieve S-II, 10' x 1/8", supplied by SUPELCO is used for the analysis of H₂, CO, CO₂, and CH₄. Water is eluted from the column at a flow rate of 30 ml/min He carrier gas, a column temperature of 150°C for 9 min, followed by a rise to 225°C achieved at a rate of 25°C/min and maintained at 225°C for 12 min.

The flow reactor test is standardized as follows: The reactor containing the carbon plus catalyst mixture is heated to 450°C at a rate of 125°C/hr in a 5 cc/min helium flow. The temperature of 450°C is maintained for 2 hours to assure complete decomposition of the catalyst nitrates and their conversion to oxides. Water flow is then started and the temperature is raised at a rate of about 10°C/min to the desired reaction temperature.

Work was carried out with graphite and with a demineralized North Dakota char.

The graphite was spectroscopic grade graphite (Ultra Carbon Corp., type UCP-2, 325 mesh) having a BET surface area of 47 m²/g. The demineralized North Dakota char had a BET surface area of 375 m²/g and
a composition of 83.35wt.% C, 0.93% H₂, 0.68% N, 0.44% S and 0.84% Cl. The chloride content is a residue from the HF/HCl demineralization.

The carbonaceous samples were impregnated by incipient wetness methods with solutions of KOH, KNO₃, Mg(NO₃)₂, or Ni(NO₃)₂ respectively. The atomic ratio of K/M²⁺ was equal to 1 and the ratio of K/C = 0.01. The samples were dried at 650°C for one hour.

In some experiments with char the catalyst was prepared first by mixing aqueous solutions of KNO₃ and Ni(NO₃)₂ or Mg(NO₃)₂ and drying. The solid catalyst was then finely ground with the char in the correct proportions.

B. Results

1) Steam Gasification of Graphite

Three different potassium oxide-metal oxide catalysts were prepared and tested. In addition to the potassium-nickel catalyst which has previously been investigated, there were two alkali-earth alkali catalysts; i.e., potassium-oxide-magnesium oxide and potassium oxide-calcium oxide.

It was found that the K-Mg catalyst was active for water dissociation at the normal gasification conditions. When the flow reactor was charged with 10⁻³ moles of this catalyst alone (no carbon present) and steam passed over the catalyst, both hydrogen and oxygen were analyzed in the products by gas chromatography. Activation energies for H₂ production and the effect of contact time are shown in Table II.
Holstein [1,2] has shown that for the type of laboratory reactor used in this work the measured activation energy \(E'\) according to

\[
E' = \frac{1}{1+n}E
\]

where \(n\) is the true reaction order in water. The rate expression is:

\[
r = k \left(\frac{pH_2O}{pH_2}\right)^n \quad 0 < n < 1.
\]

On the basis of published data, an order of \(n = 0.5\) can be assumed and Table 1 shows the true activation energy for each catalyst. The values in Table 1 are indicative of a non-catalytic controlling step.

Fig. 2 shows the molar rate of gas production \((\text{H}_2\text{ and CO}_2)\) for each of these catalysts as a function of time at 660°C. After an initial non-steady state (declining activity) period of several hours, a steady state and a constant rate is observed.

Of the catalysts tested, the Ni-K catalyst has a longer non-steady state period than the others but arrives at about the same steady state level. The difference may be due to changes in the oxidation state of the nickel. The alkali-earth alkali catalysts reach steady state conversion faster. The K-Mg catalyst is about twice as active as K-Ca.

Fig. 3 shows the \(\text{H}_2\) evolution during the non-steady-state period and compares the three catalysts. Amounts of \(\text{H}_2\) and \(\text{CO}_2\) produced according to the stoichiometry

\[
\text{C} + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{CO}_2
\]

are only observed in the case of the less active K-Ca catalyst. \(\text{H}_2/\text{CO}_2\) ratios greater than 2 are observed for K-Mg and for K-Ni and are attributed to greater water splitting activity with hydrogen being
liberated and oxygen oxidizing some of the carbon. Selectivities to \( \text{H}_2 \), CO, \( \text{CO}_2 \), and \( \text{CH}_4 \) show no great variation over the range of conditions tested (580 – 700\(^\circ\)C; water molecular space velocities 50 – 500 hr\(^{-1}\)). The space velocity also showed no major effect on the total rate of gas production.

2) Steam Gasification of Demineralized North Dakota Char with K-Mg, K-Ni and Mg-Ni Catalysts

In view of the large surface area and of the porosity of chars, catalyst dispersion on the char surface can vary substantially and measured gasification rates are not necessarily characteristic of the behavior of each catalyst. It has previously been shown [3] that the wetting properties of catalysts are an important factor in explaining their activity for steam gasification.

In the present work catalysts were prepared separately by premixing solutions of the metal nitrates and drying to solids. Mixtures of K-Ni nitrates and of K-Mg nitrates melted at about 80\(^\circ\)C, while Ni-Mg nitrate remained solid. The solid catalysts were then incorporated into the char as described in the "Experimental" section of this report.

Fig. 4 plots the total gas production as a function of time for each catalyst and the greater activity of K-Ni and of K-Mg compared to Mg-Ni may indicate greater mobility and wetting properties of these catalysts. Total conversion of carbon after 3 hours with K-Ni is about the same as after 4 hours with Mg-K and after 10 hours with Mg-Ni. Catalysts used in this graph were mechanically mixed with char and the initial drop in gasification is probably an initiation period to liquify the catalyst and wet the char.
Fig. 5 presents the product distribution ($H_2$, $CO$, $CO_2$) as a function of carbon conversion. The selectivity for $H_2$ with both K-Mg and K-Ni exhibits the same behavior that was observed when solutions for these catalysts were impregnated on graphite. The $H_2/CO_2$ ratio is greater than 2 up to about 70% conversion. The ratio then drops as less and less carbon is available, probably because of a lack of carbon to react. It is interesting to note that the amounts of CO (and of $CH_4$) produced while small, are larger than in the case of graphite. It thus appears that while the selectivity to $H_2$ is only a function of the catalyst used, selectivity to CO and $CO_2$ can vary with the type of carbon. The activation energy for K-Mg and for K-Ni with this char is 234 KJ/mol, lower than the activation energy for the graphite case shown in Table I.

Delannay et al [4] in discussing earlier work in this project had proposed the reaction scheme shown below:

1. $K_2O + H_2O \rightarrow 2KOH$
2. $2K-O-H + C_s \rightarrow 2K-O-C + H_2$
3. $2K-O-C \rightarrow K_2O + [>C(O)]_s$
4. $[C(O)]_s \rightarrow CO_2$ or $CO$

with the rate controlling step being equation (4). The results presented in this report support this scheme. The production of CO or $CO_2$ will depend both on the nature of the carbon to be gasified and on its oxidation state, which in turn is determined by the reaction with oxygen from water dissociation.

In the case of K-$M^{2+}$ catalysts the following steps can also be suggested:

5. $2KOH + M^{2} \rightarrow MO + K_2O + H_2$
6. $MO + C_s \rightarrow M^{2} +[C(O)]_s$
7. $M^{2} + H_2O \rightarrow MO + H_2$
This scheme would support the observations that:

i) $\text{H}_2/\text{CO}_2$ ratios are higher than 2 at carbon conversions up to about 70% and lower than stoichiometric at very high carbon conversion.

ii) There is high non-catalytic activation energy for steam gasification of graphite and of char and low activation energy for water dissociation on the K-Mg catalyst.

V. Future Work

Previously tested catalysts will be used for the steam gasification of chars of different ash content and composition. Catalyst deactivation and means to inhibit it will be investigated. New catalyst compositions will be used to overcome poisoning problems on the basis of a better understanding of catalyst-ash interaction.

IV. References


(2) W.L. Holstein and M. Boudart, J. Cat., 75, 337 (1982).


TABLE I

ACTIVATION ENERGIES FOR THE DIFFERENT CATALYSTS TESTED

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ea Global App. KJ/mol</th>
<th>Regression Factor Min. Squares (6 values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-Ni</td>
<td>279.0</td>
<td>-0.988</td>
</tr>
<tr>
<td>K-Ca</td>
<td>275.9</td>
<td>-0.998</td>
</tr>
<tr>
<td>K-Mg</td>
<td>282.1</td>
<td>-0.997</td>
</tr>
</tbody>
</table>

TABLE II

Water dissociation on K-Mg catalyst alone
K/Mg = 1 Water flow during measuring Ea = 1.44 ml/min
Carrier gas Ar: 2.75 mol/min Temp range: 582 - 700°C
Contact time variation T = 700°C

<table>
<thead>
<tr>
<th>H₂ (counts)</th>
<th>78192</th>
<th>67501</th>
<th>69534</th>
<th>E.a. App.</th>
<th>regression factor for Ea min squares (4 points)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact time (min)</td>
<td>0.694</td>
<td>3.759</td>
<td>18.87</td>
<td>132 KJ/mol</td>
<td>-0.988</td>
</tr>
</tbody>
</table>

Chromatographic conditions:

Carrier: N₂ 65cc/min; Det T.C.D. Temp = 200°C,
Att. 1 Range 0

Column Carbosieve S-II Temp = 100°C
FIGURE 1 EXPERIMENTAL SETUP

1. Sample
2. Oven
3. Temperature control
4. Temperature indicator
5. Pressure gauges
6. Mass flow controller
7. Syringe pump
8. He 99.99% bottle
9. Expander
10. Water recipient
11. Calibrating mixture for G.C.
12. Bubble flowmeter
13. Gas sample valve
14. Gas chromatograph

△ : Valve
□□□□ : Wire heater
FIGURE 2

TOTAL RATE vs TIME OF REACTION

for steam gasification of graphite

T = 933 K
P = 15 PSI

MOLAR RATIO

$K^+ \quad M^{2+} \quad C$

0.01/0.01/1

- \quad K-Mg

\triangle \quad K-Ni

\square \quad K-Ca
$T = 933K$
$P = 15 PSI$

MOLAR RATIO

$K^+ \cdot M^{2+} \cdot C$

0.01/0.01/1

Figure 3 HYDROGEN SELECTIVITY vs CONVERSION

for steam gasification of graphite
FIGURE 4  TOTAL RATE vs TIME OF REACTION
for steam gasification of North Dak. char demineralised
Figure 5: Selectivity vs Conversion
for steam gasification of North Dakota char demineralised