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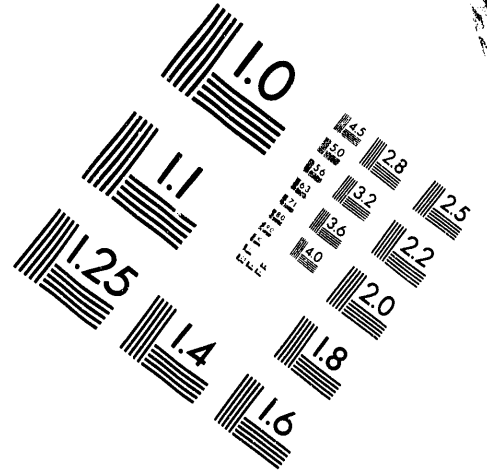
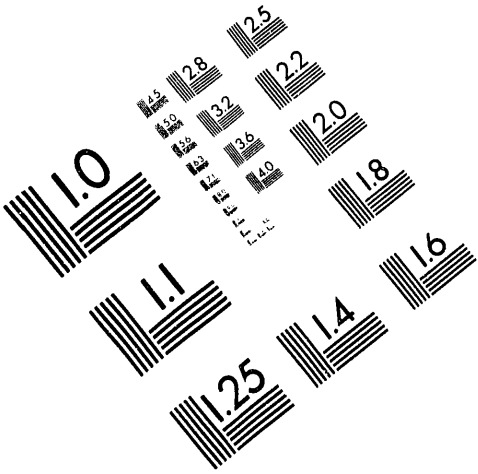
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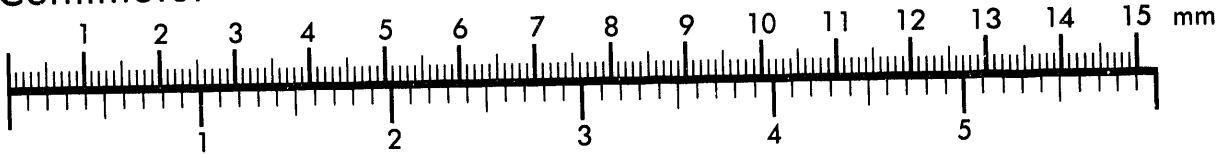
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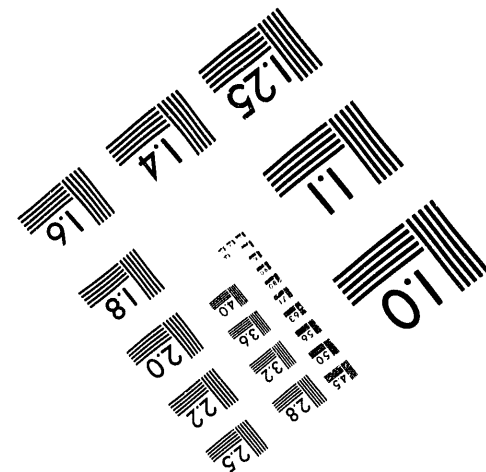
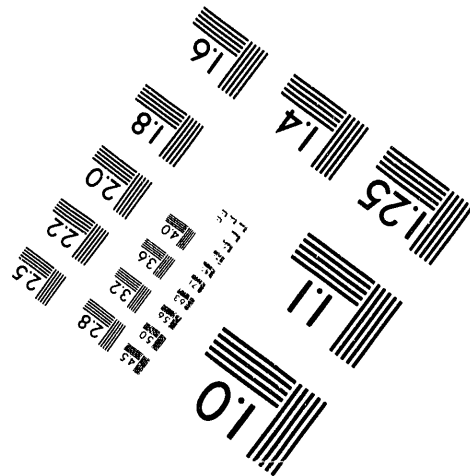
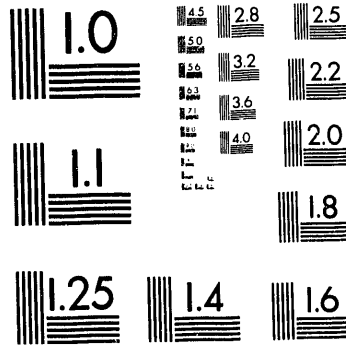
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QUARTERLY REPORT

July 1, 1992 - September 30, 1992

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

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I. Task Description for FY 1992

Work will continue on the oxidative coupling reaction of methane over ternary oxide catalysts to produce C₂, C₃ and C₄ hydrocarbons and particularly olefins with high selectivity. The work which has shown that close to 100% selectivity can be obtained has received wide attention and has resulted in collaborative efforts with industry (CRADA) towards the development of a commercial process. An immediate purpose of additional work is to increase the conversion without diminishing the extremely high selectivity of the reaction and also to permit operation at higher space velocity to reduce equipment size. The mechanism of this reaction is not understood and much additional work is needed to explain the role of carbon formation and of water as intermediates in the reaction and to investigate whether carbon oxides are intermediates. It has been found that oxides other than calcium-nickel-potassium oxides can be useful catalysts for this reaction in the presence of steam and at relatively low temperatures and long contact times. Better definition of the class of binary metal oxides is required and better catalyst characterization is needed to ensure reproducibility of catalyst preparation and operational results. Pretreatment of the catalyst should be shortened and higher space velocities must be obtained. Close collaboration with Orion ACT is required to advance the project toward the pilot plant stage. In the area of coal and char catalytic steam gasification, the large volume of data obtained at atmospheric pressure will be extended to operations at higher pressures.

II. Introduction

At the request of the Morgantown Energy Technology Center, two previously separate projects (a) *Fundamental Studies of Gasification* and (b) *Synthesis and Characterization of Catalysts for Gasification of Carbonaceous Materials* were combined for funding purposes. This is the third quarterly report of the combined project. The principle investigators for part (a) remain Heinz Heinemann and Gabor A. Somorjai and for part (b) Dale L. Perry.

Active collaboration with Orion ACT under the CRADA was continued during the report quarter.

III. Highlights

- a) *Catalytic Steam Gasification of Coals and Cokes*
 - Char from Illinois #6 coal was steam gasified at 640°C in the presence and absence of K-Ca oxide catalyst at both atmospheric and at 100 psig pressure.

- The catalyst containing char gasified at about twice the rate as the char alone. Operating at elevated pressure gave a very minor improvement of rate.
- Hydrogen production rate corresponded to the gasification rate. Methane and CO production were lower at higher pressure.
- Charring coal in the presence of small amounts of caustic resulted in a char that could be gasified at about twice the rate of the normal char. The relationships of catalyzed vs. thermal gasification and atmospheric vs. 100 psig pressure were unchanged.

b) Oxidative Methane Coupling

- An error in the previously obtained mass balances was corrected by introducing an internal standard into the feed stream to the reactor.
- The calcium oxide in the catalyst progressively sorbs some CO₂ as evidenced by x-ray diffraction measurements.
- Catalyst regeneration with oxygen at 680°C for 18 hrs. decomposes about one-half of the carbonate. Regeneration with oxygen and steam decomposes all of the carbonate.
- Corrected mass balances show higher conversion of methane and lower selectivity to higher hydrocarbons than before, with somewhat lower C₂⁺ yields.
- The previously described effect of steam in slightly reducing conversion and greatly increasing selectivity were confirmed.

c) Synthesis and Characterization of Catalysts

- Coupling catalysts of the CaNiK oxide type were studied by magnetochemical techniques. Potassium dioxide (KO₂) was found in significant amounts. Results were correlated to x-ray spectra.
- Ca(OH)₂ was found to be present in the catalysts and was confirmed by Fourier transform infra red spectroscopy.

IV. Progress of Studies

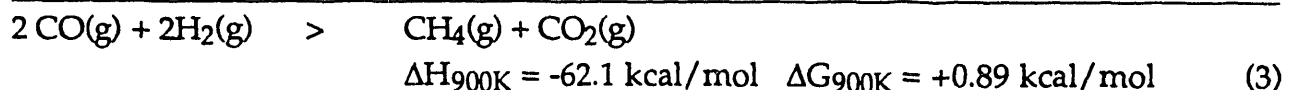
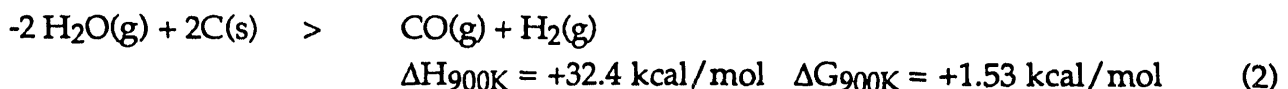
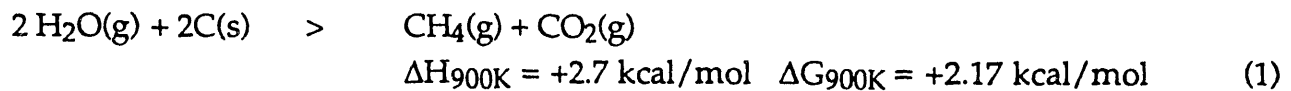
a) Catalytic Steam Gasification of Coals and Cokes

Chars and cokes were tested in the new high pressure gasification unit. The effect of pressure was evaluated for one char, both in the absence and presence of catalyst. The effect of charring coal in the presence of caustic was also determined.

Chars were obtained by heating Illinois #6 coal (Argonne Premium, high volatile bituminous) at 10°C/min to 500°C and holding for 2 h. For chars obtained in the presence of caustic, a solution of NaOH (21 wt%) was added to the coal (8.5% of the coal weight) prior to heating. The K-Ca catalyst was added to the chars by impregnation with solutions containing equimolar amounts of KNO₃ and Ca(NO₃)₂·4H₂O, followed by drying at 200°C for 10 h. Catalyst loading was K:Ca:C = 1:1:100 assuming 80 wt% C in the char.

Heating of the coal in the absence of NaOH produced a solid mass of char which was slightly swollen. Small difficulties were encountered when crushing this char, and when mixing with the impregnating solution. Heating in the presence of NaOH produced a less swollen char that had a lower crush strength and improved mixing with the impregnating solution as compared to the char obtained without NaOH.

Figure 1 is a graph of the carbon conversion versus time, showing the effects of catalyst and pressure on the gasification of chars obtained in the absence of NaOH. It is apparent that the catalyzed chars react over twice as fast as the uncatalyzed chars. The increase in conversion stems from an increase in H₂ and CO₂ production (illustrated in Figure 2 for H₂ production). Pressure is seen to have a small enhancing effect on the uncatalyzed char and no apparent effect on conversion or the major products of the catalyzed char. It does seem to affect the relative amounts of the minor products CO and CH₄, with are produced in quantities that are an order of magnitude lower than H₂ and CO₂. Figure 3 shows the production rate of CO and methane as a function of time for the catalyzed char. The production of CO is depressed at 100 psig, while methane production is enhanced, and by roughly half the amount of the depression in CO. This could occur through the following reactions:



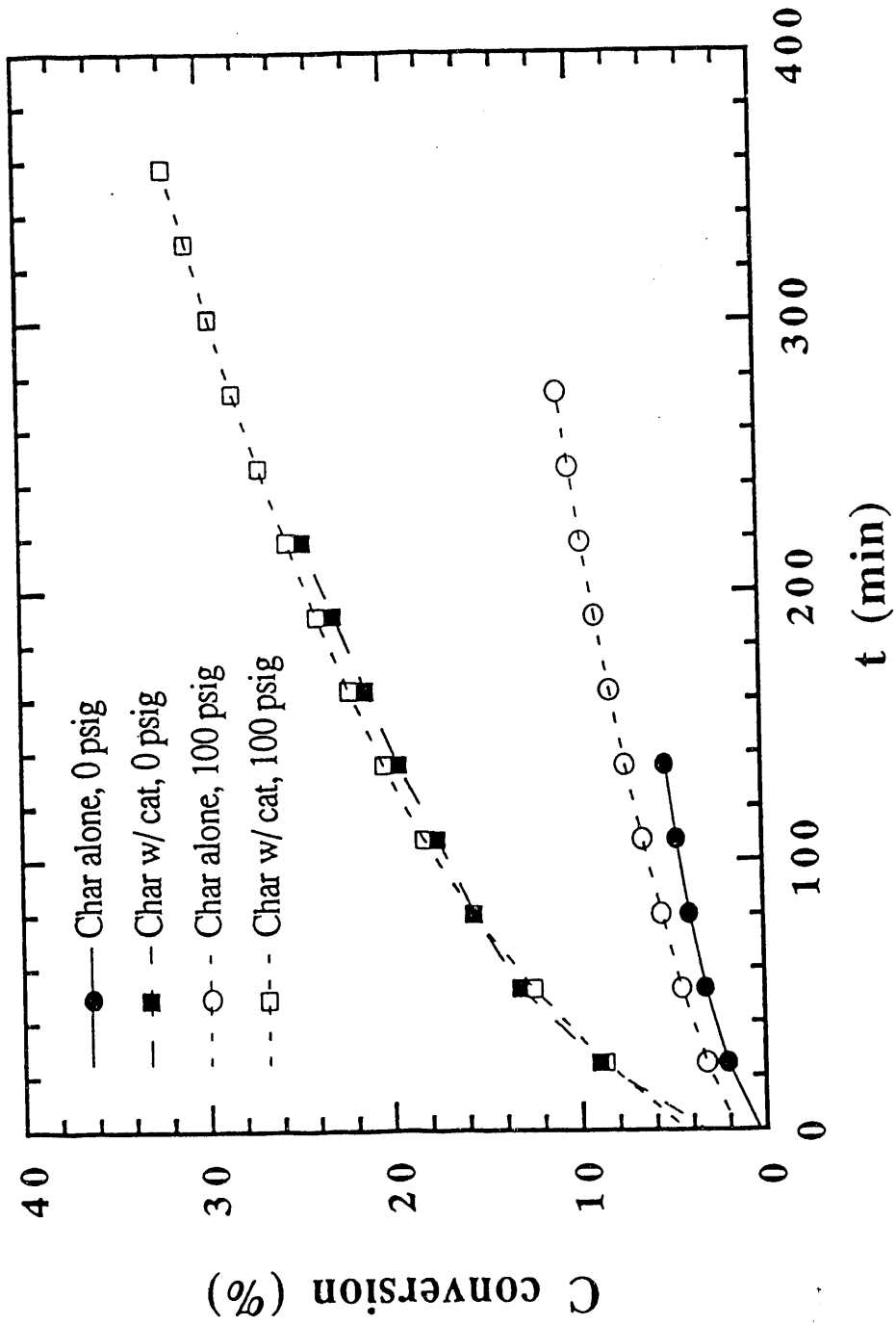


Figure 1

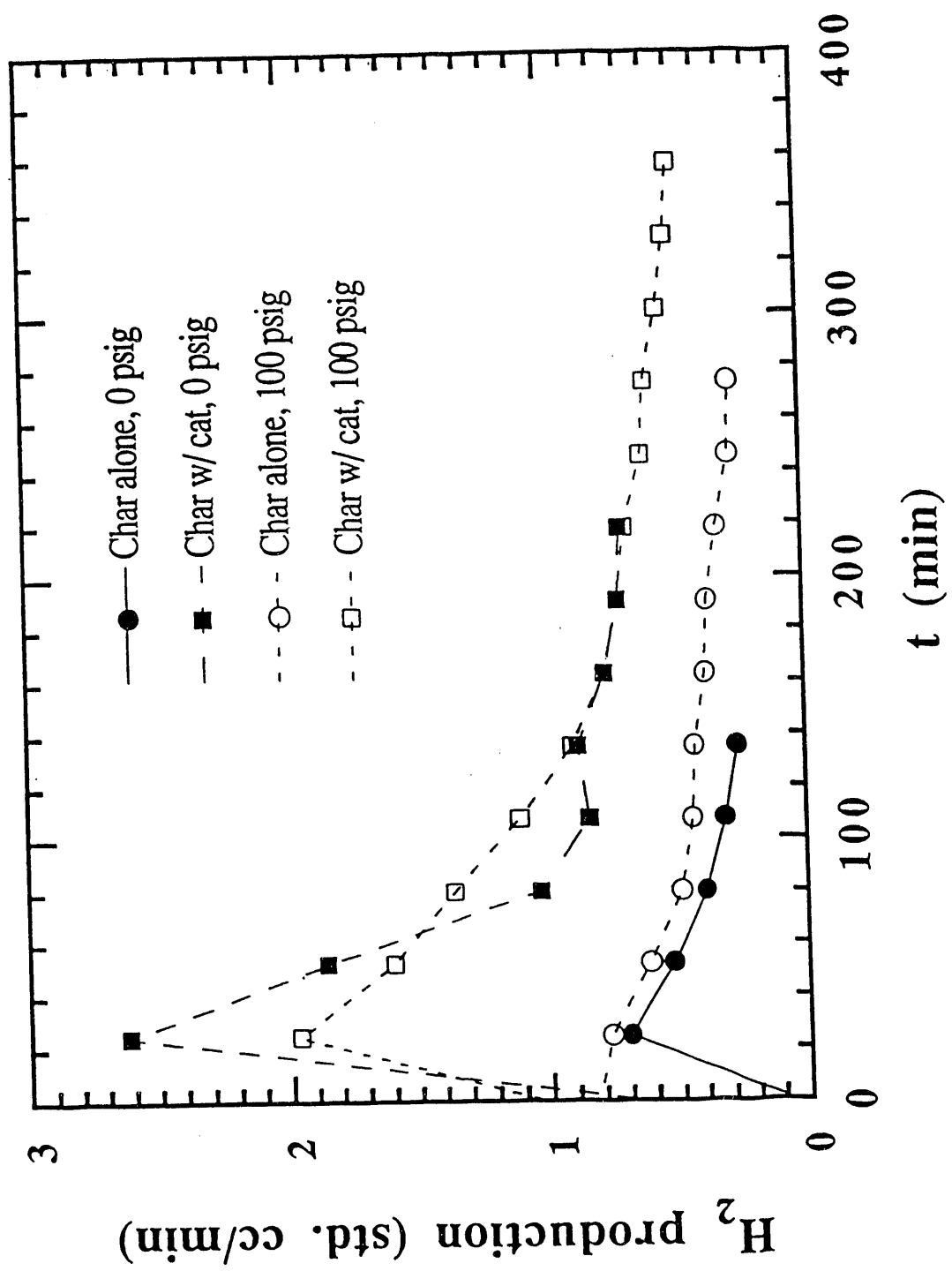


Figure 2

Catalyzed Char

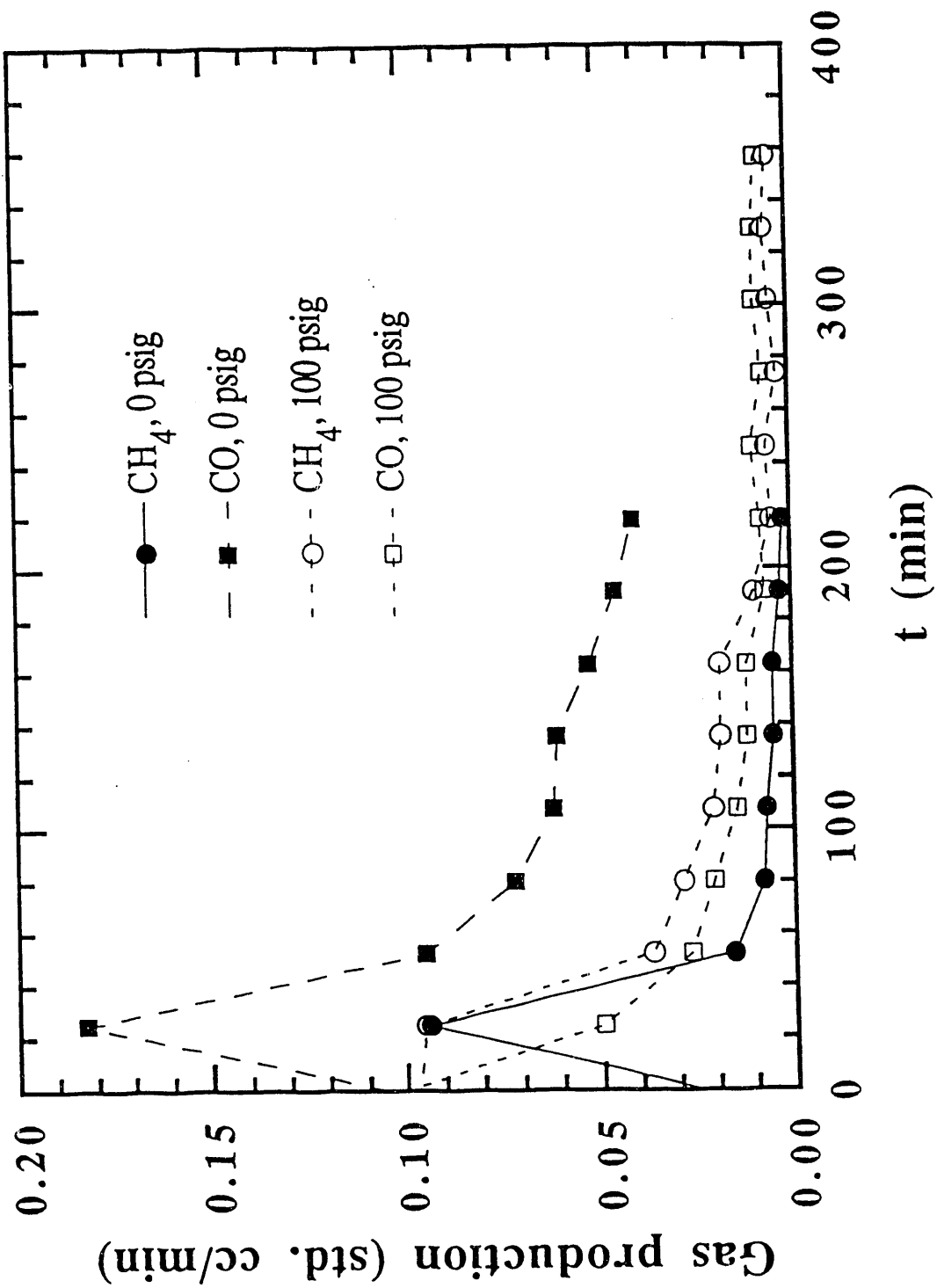


Figure 3

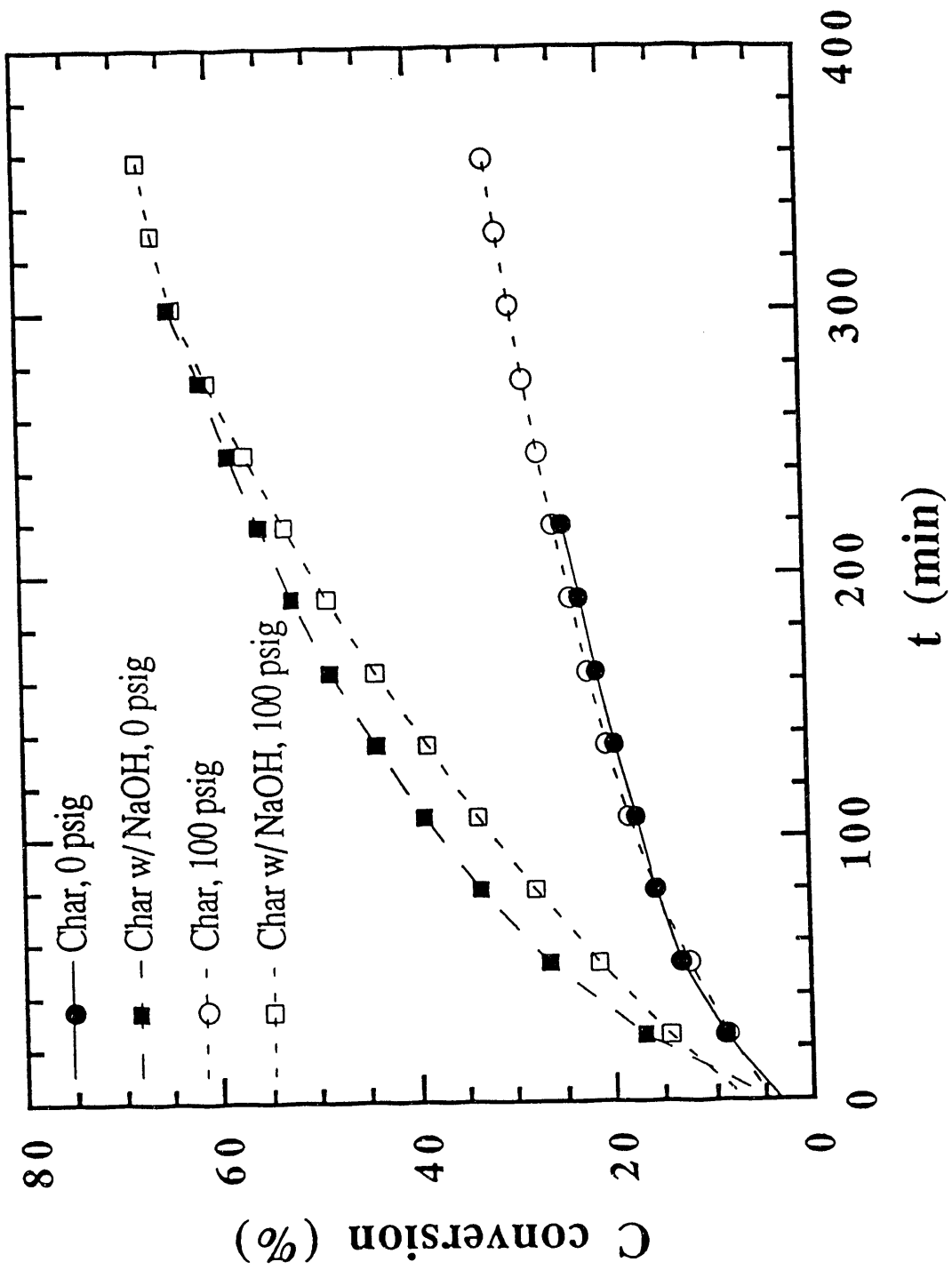


Figure 4

Chars Prepared in the Presence of Caustic

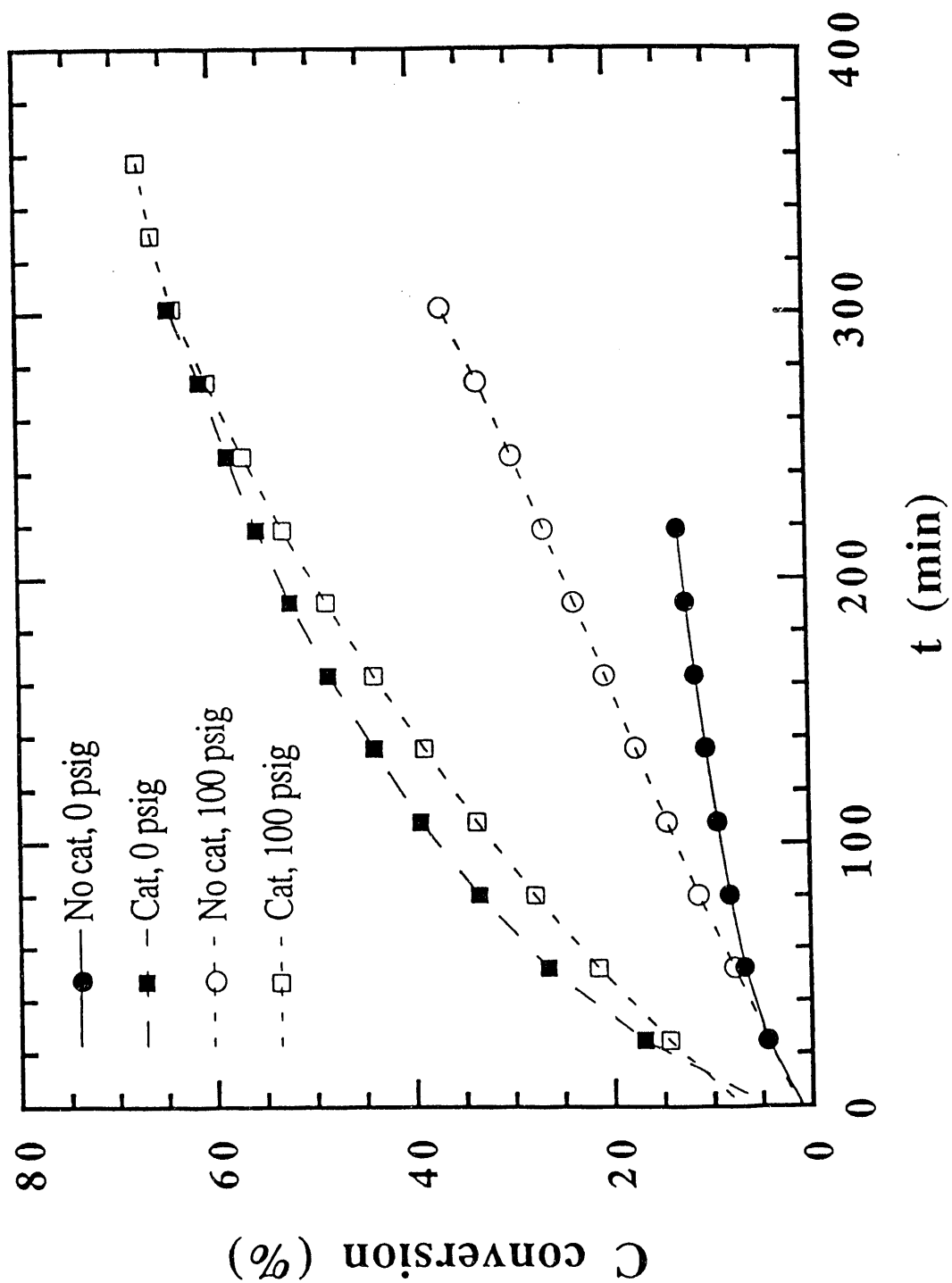


Figure 5

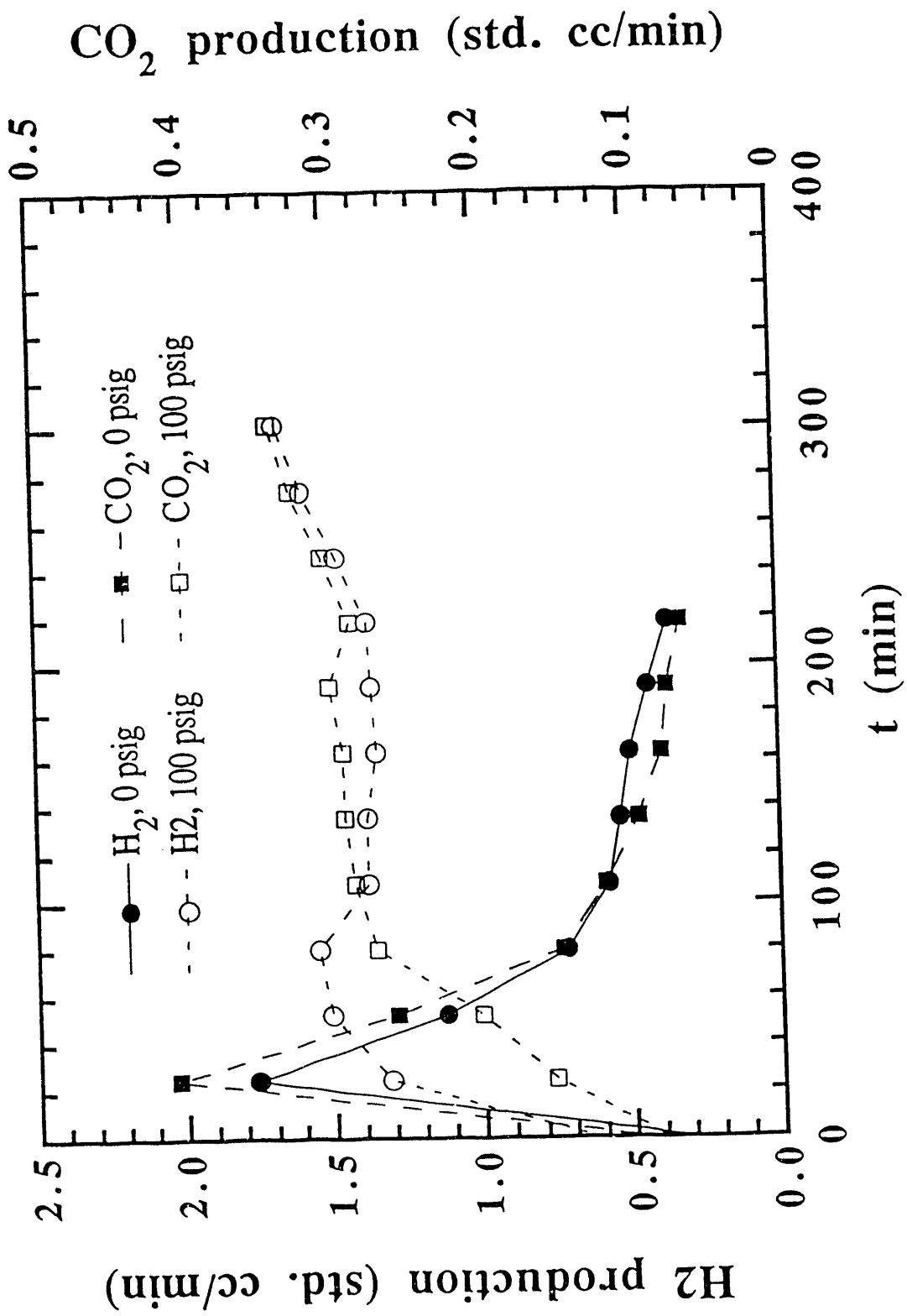


Figure 6

in which the overall equation (eq. 3) has a decrease in gas phase moles, which would be more favored at high pressure.

Figure 4 is a graph of conversion vs. time which illustrates the effect of pressure and charring in the presence of NaOH on the gasification of catalyzed chars. Charring with caustic is shown to enhance the reactivity of the catalyzed char by another factor of 2 over the plain catalyzed char.

Figure 5 compares the conversion at different pressures for the gasification of catalyzed and uncatalyzed chars prepared in the presence of caustic. The same effect of catalyst is seen as in Figure 1 and pressure has a positive effect on the gasification of the uncatalyzed char. This increase in conversion is due to the sustained production of hydrogen and CO₂ as shown in Figure 6.

The major effect of charring a coal in the presence of caustic parallels the findings for petroleum coke and is probably generic (reference Jan. 1, 1992, quarterly report, LBL-32005).

b) Oxidative Methane Coupling

Recently, an error was discovered in the mass balance of earlier work using CaNiK oxide and MgO-Li oxide catalysts. This was due to some CO₂ produced in the reaction being sorbed, against previous evidence, on the catalyst. An internal standard (nitrogen) has been introduced to correct results. Methane on the inlet side can be related to this standard, as can methane, CO₂, and C₂⁺ hydrocarbons on the outlet side, giving a reliable mass balance. Differences between inlet and outlet weights are then due to CO₂ sorbed on the catalyst.

Catalysts of the composition Ca₃NiK_{0.1}O_x were made by mixing and grinding CaO, NiO and KNO₃ powders followed by activation in flowing oxygen at 680°C for 18 h. The catalysts were reacted at 600°C in a mixture of methane, oxygen and steam (3:1:6.5 molar ratio) for 1.5, 3.0 and 6.8 hours. X-ray diffraction was performed on the used catalyst. The formation of bulk calcium carbonate with the calcite structure was observed, the amount of which grew as the reaction progressed. Figure 7 shows the amount of CaCO₃ in the catalyst as a function of time on stream. This increase must occur through the formation of CO₂ in the gas phase which then reacts with the CaO to form CaCO₃. No appreciable Ca(OH)₂ was observed in the XRD patterns.

This formation of bulk carbonate was related to the catalyst deactivation described in one of the previous studies [3], which also found that the deactivated catalyst could be reactivated by treatment with oxygen or oxygen plus steam at 680°C. We have now looked to see if the activation and regeneration conditions were sufficient to decompose bulk CaCO₃ formed during the reaction. Table 1 shows the decomposition of carbonate as observed by XRD for two used catalysts.

Table 1: Catalyst Regeneration (XRD)

| Catalyst | CaCO ₃ /(CaO+CaCO ₃) | | % CaCO ₃ Decomposition |
|--|---|------|--------------------------------------|
| | Ratio | | |
| Deactivated | 0.40 | 0.44 | -- |
| Regenerated (O ₂ ,680°C) | -- | 0.23 | 48 |
| Regenerated (O ₂ ,H ₂ O,680°C) | -- | 0.01 | 98 |
| Regenerated (O ₂ ,H ₂ O,600°C) | 0.35 | -- | 11 |

Regeneration in 2.5 cc/min oxygen at 680°C overnight (activation conditions) decomposed about half of the carbonate. Regeneration at 680°C in oxygen and steam decomposed essentially all of the carbonate. Treatment at 600°C in oxygen and steam (operating temperature) decomposed just over 10% of the carbonate. The greater decomposition at the higher temperature can be explained by the higher decomposition pressure of CO₂ over CaCO₃ (~16 mm Hg at 680°C vs. ~2 mm Hg at 600°C). The presence of steam is not expected to affect this equilibrium, as the temperature is above that needed to dehydrate Ca(OH)₂, the absence of which is confirmed by XRD. Steam can then act only to enhance the diffusion of bulk carbonate to the surface and/or to help carry the CO₂ away in the effluent. The decomposition of carbonate may then explain the regeneration of catalyst performance upon high temperature treatment.

In order to form the quantity of carbonate observed in the XRD, considerable deficits in both the carbon and oxygen balances must be observed. Upon re-examination of earlier work and of the experimental unit, an error was discovered in the measurement of the reactor effluent which led to erroneous material balances. In order to obtain proper balances, the equipment was modified such that nitrogen could be used as an inert internal standard. The results of a typical run using the internal standard are shown in Table 2.

**Table 2. Oxidative Methane Coupling; Ca₃NiK_{0.1}O_x catalyst
Mixed Oxides; Activation - O₂, 680°C, 18 h
Rxn - CH₄:O₂:H₂O = 3:1:6.5, 4.0 mmol CH₄/g cat/h, 600°C**

| Time, hrs | CH ₄ conv. % | C ₂₊ | Selectivity, % | | C Balance % |
|--------------|----------------------------|-----------------|-----------------|----------------------------|----------------|
| | | | CO ₂ | Undetected in Gas Phase | |
| 1.5 | 21 | 16 | 1 | 83 | 82 |
| 2.5 | 20 | 15 | 2 | 83 | 83 |
| 5.5 | 20 | 11 | 3 | 86 | 83 |
| 7.5 | 19 | 8 | 33 | 59 | 89 |
| 11.5 | 19 | 7 | 51 | 42 | 92 |

The composition of detectable products in the gas phase (hydrocarbons and CO_x) show the same ratio as previously observed (80-90% C₂₊), however, much more

methane reacts than can be accounted for in gas phase products. The deficits in the carbon and oxygen balances (~17 and 93%, respectively in the first 6 h) must then reside in those products that are not detected in the outlet stream. The consumption of methane and oxygen for the formation of solid carbonate is in a ratio that is consistent with the deficits in the gas phase C and O balances. However, the formation of coke cannot be entirely excluded. After the first 6 h, the solid can no longer absorb CO₂ as fast as it is created, so the amount of CO₂ detected in the gas phase increases, and the deficits in the material balances decrease, indicating that less CO₂ reacts to form solid carbonate.

When comparing the reaction in the presence and absence of steam, we observed that the methane conversion increased when steam was replaced by helium, but the selectivity to hydrocarbons dropped to zero, and CO was observed in the gas phase (see Table 3).

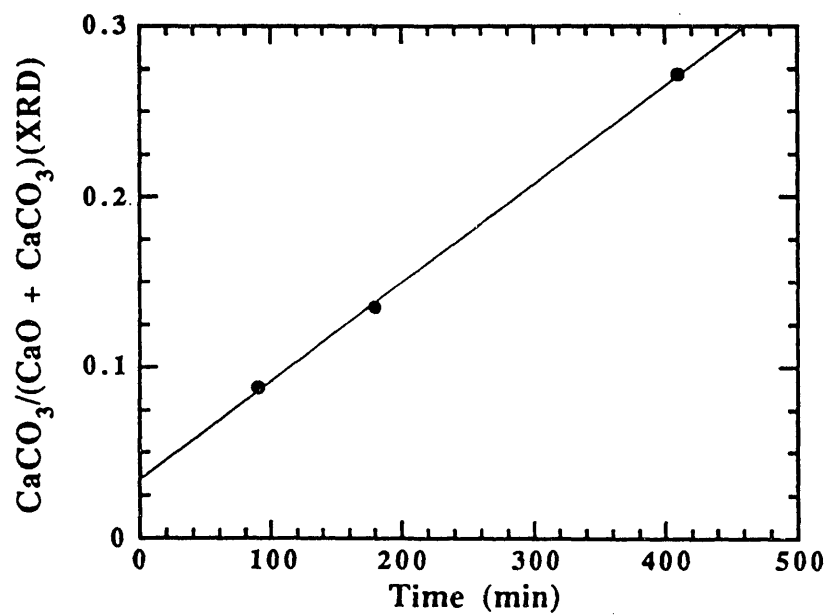
**Table 3: Oxidative Methane Coupling; Ca₃NiK_{0.1}O_x catalyst
Mixed Oxides; Activation - O₂, 680°C, 18 h
Rxn - CH₄:O₂:H₂O(or He) = 3:1:6.5, 4.0 mmol CH₄/g cat/h, 600°C**

| Time hrs | Conv. % | Presence of Steam | | | C Balance | Conv. % | Absence of Steam | | | C Balance |
|-------------|------------|-------------------|-----------------|-------------|--------------|------------|------------------|-----------------|-------------|--------------|
| | | Selectivity, % | | | | | Selectivity, % | | | |
| | | C ₂₊ | CO _x | Undet. % | | | C ₂₊ | CO _x | Undet. % | |
| 1.5 | 21 | 16 | 1 | 83 | 82 | 48 | 0 | 10 | 90 | 56 |
| 2.5 | 20 | 15 | 2 | 83 | 83 | 54 | 0 | 7 | 93 | 51 |
| 5.5 | 20 | 11 | 3 | 86 | 83 | 58 | 0 | 43 | 57 | 67 |
| 7.5 | 19 | 8 | 33 | 59 | 89 | 58 | 0 | 48 | 52 | 70 |

The presence of steam must then play some role in the formation of hydrocarbons, possibly by partially hydroxylating the catalyst surface. A more likely explanation is that steam can act as a gas phase radical trap and interrupt the chain reaction of methane combustion to CO_x. This can serve to extend the life of methyl radicals in the gas phase, thus increasing the likelihood that they will couple to form ethane. In the absence of steam, it appears that the NiO is reduced to Ni metal, which then becomes a good catalyst for producing CO from methane. The poor carbon balances can then be attributed to the accumulation of carbon deposits, which is common when methane reacts with Ni in the absence of steam.

If the carbonate CO₂ is included in the outlet stream, the product distribution in the presence of steam falls in line with what is predicted by reaction mechanisms which include gas phase coupling of radicals which are produced by the activation of methane on the catalyst surface [4]. This mechanism also explains the absence of D-substituted hydrocarbons when D₂O was used instead of water in the reaction [2,3].

Figure 7
Carbonate Accumulation in $\text{Ca}_3\text{NiK}_{0.1}\text{O}_x$ Catalysts
X-ray Diffraction



c) *Synthesis and Characterization of Catalysts*

Studies continued in using magnetochemical techniques to gain a better understanding of the differences between individual catalysts composed of potassium, nickel, and calcium oxides. Attempts were made to correlate the magnetic data with other experimental data, with the most emphasis on the x-ray diffraction data which yield unequivocal documentation of species in the catalytic samples. The magnetochemical data most closely correlated with the amount of potassium dioxide, KO_2 , in the samples in which this compound was in significant amounts.

Other studies centered on the different compounds that could be found in catalysts and their ratios to one another. Several compounds that had previously been documented in the x-ray diffraction patterns of the catalysts continued to be observed, including NiO and CaO; also, the hydrated form of the CaO--Ca(OH)₂--was observed. The hydration reaction of oxides to form this type of compound was further documented by Fourier transform infrared spectroscopy in which sharp infrared bands in the 3400-3500 cm^{-1} region are always observed. These bands are extremely sharp, non-diffuse ones, clearly indicating the absence of hydrogen-bonded bulk water species.

Rigorous magnetochemical studies were conducted on potassium dioxide, KO_2 , and the results were in good agreement with those isolated reports in the research literature. The inherent paramagnetism of this compound is due to the O_2 species rather than the diamagnetic K^+ ion.

Further studies were done on NiO to gain a better understanding of its paramagnetism as a function of particle size. The magnetic curves have been shown to be a function of this size. Also, the chemistry of the particles changes as they grow smaller (nanometer level sizes).

References

1. Pereira, P., Lee, S.H., Somorjai, G.A., and Heinemann, H., Catal. Letters, 6(1990), 255.
2. Rasko, J., Pereira, P., Somorjai, G.A., and Heinemann, H., Catal. Letters, 9(1991), 395.
3. Rasko, J., Somorjai, G.A., and Heinemann, H., Applied Catal. A, General, 84(1992), 57.
4. Lunsford, J.H., Catal. Today, 6(1990, n.3), 235.

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