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Fundamental Studies of Catalytic Gasification. Quarterly Report: April 1-June 30, 1992

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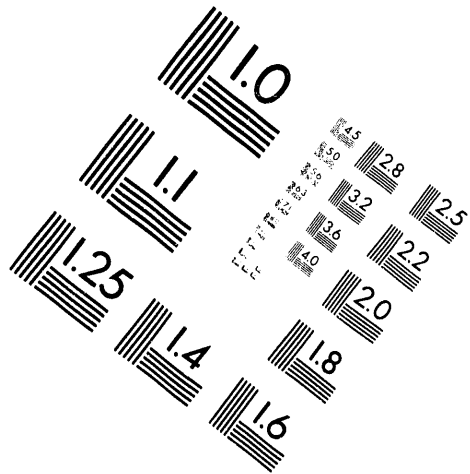
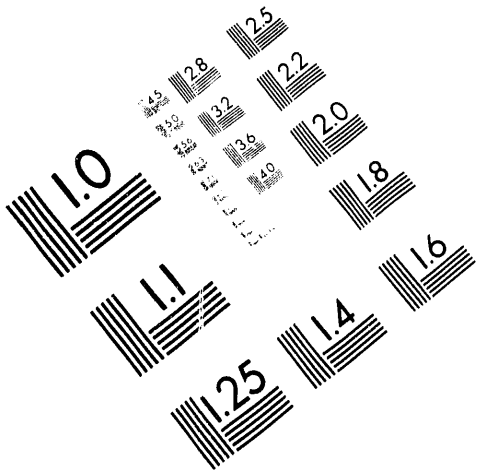
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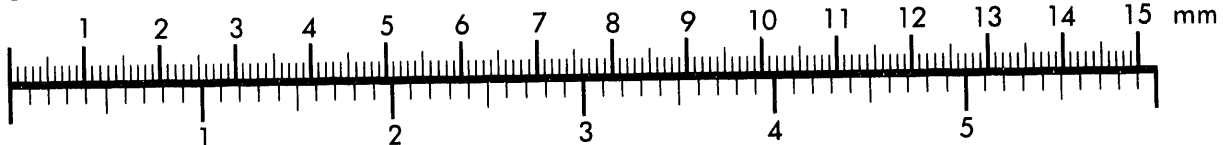
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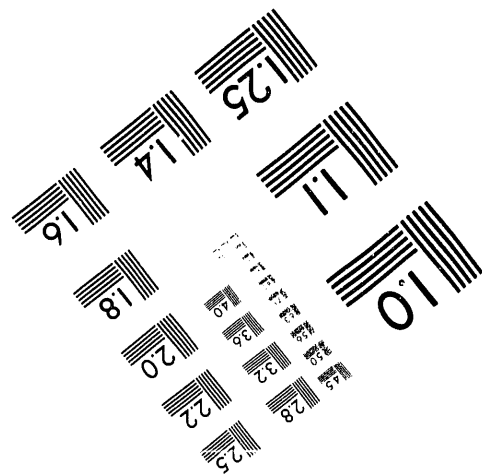
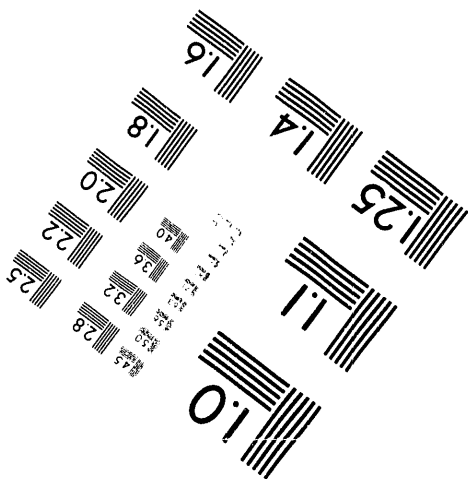
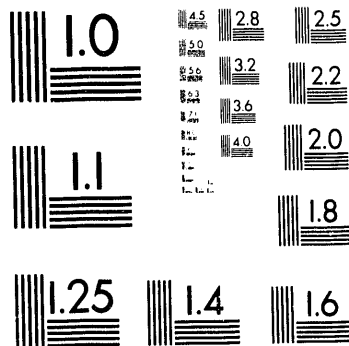
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QUARTERLY REPORT

April 1, 1992 - June 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 second 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. Orion has started work in their laboratories in Delaware after assembling and building equipment. Operation of units in both Orion's lab and LBL are currently being checked against each other. A system for information exchange has been established.

III. Highlights

- a) *Catalytic Steam Gasification of Coals and Cokes*
 - The new pressure unit is operative, but insufficient data have been obtained to draw conclusions on the effect of pressure on gasification

b) Oxidative Methane Coupling

i.) Lithium-Magnesium Oxide Catalysts

- We have shown that lithium-magnesium oxide catalysts operating under the same conditions as Ca-Ni-K oxide catalysts can give 90% selectivity to C₂₊ hydrocarbons at 10-12% conversion. This is much higher than described in the literature for this type of catalyst at higher temperatures and higher space velocity.
- The presence of steam has been shown to be essential for high selectivity and conversion.
- The reaction is very sensitive to the method of catalyst preparation and catalyst activation. Good catalysts were prepared from the precursor nitrates. Catalysts prepared from oxides or carbonates were much less active.
- The presence of lithium in the catalyst is important. Substituting potassium for lithium results in a significant decrease in selectivity.
- Incorporation of a transition metal oxide into the catalyst did not improve its performance.
- A patent application has been filed.

i.i.) Ca-Ni-K Oxide Catalysts

- An x-ray diffraction study of fresh and deactivated catalysts showed a major increase in CaCO₃ content of the deactivated catalyst. It is not yet clear at what stage of operation the carbonate formation occurred.
- The CaCO₃ content of the deactivated catalyst is greatly reduced by treatment with oxygen at 680°C and is essentially eliminated by treatment with oxygen and steam at this temperature.
- Hydrocarbon selectivity to C₂₊ was not affected by particle size variation as long as the particle size was less than 0.2mm.

c) Synthesis and Characterization of Catalysts

- Freshly prepared and used catalyst samples have been analyzed by different spectrographic techniques.
- Differences were found between the fresh and the used Ca-Ni-K-O_x catalyst. Fourier transform infrared spectra, x-ray diffraction, and XPS data indicate CaCO₃ formation as well as changes in the nickel spectrum.

IV. Progress of Studies

a) *Catalytic Steam Gasification of Coals and Cokes*

The new pressure unit has been taken into operation. A flow diagram is shown in Figure 1. Insufficient data have been obtained as yet to allow conclusions on the effect of pressure. An early objective in addition to the effect of pressure) will be to investigate whether the findings of greatly increased gasification rate when cokes are prepared in the presence of caustic (ref. January 1, 1992 quarterly report, LBL-32005) can be extended to chars which have been prepared from coals in the presence of caustic. For this purpose, we have obtained a series of coals from the coal bank at Argonne National Laboratory.

b) Oxidative Methane Coupling

i.) *Lithium-Magnesium Oxide Catalysts*

Previous work in this laboratory has shown that oxydehydrogenation of methane to hydrocarbons over a calcium-nickel-potassium oxide catalyst can occur with high selectivity (>90%) at temperatures $\leq 600^{\circ}\text{C}$. It has demonstrated that the presence of steam is essential for high selectivity to hydrocarbons. We now report the catalytic oxidative coupling of methane to C_2 and higher hydrocarbons over magnesium-lithium oxide catalysts at low temperatures ($\leq 600^{\circ}\text{C}$) and low space velocity. Our results show that under conditions similar to those used with Ca-Ni-K oxide catalysts, Mg-Li-O catalyst is able to facilitate the oxydehydrogenation of CH_4 to give 10-12% conversion with selectivity to hydrocarbons close to 100%. It seems possible that introduction of steam into the reaction mixture of methane and oxygen can result in a significant decrease of the reaction temperature required for the oxidative coupling of methane when coupled with long contact times. This may be a general phenomenon for catalysts which show high activity and selectivity for the oxidative coupling of methane at high temperatures ($\geq 700^{\circ}\text{C}$) and short contact times. It should be pointed out that since its discovery by Lunsford et al. Li/MgO has been intensively studied for its activity in facilitating the oxidative coupling of methane at temperatures $\geq 700^{\circ}\text{C}$. This is the first time it has been shown that the oxydehydrogenation of methane in the presence of steam to hydrocarbons with very high selectivity can occur over lithium-containing magnesium oxide catalyst at low temperature. A patent application has been filed.

Experiments were carried out using ~ 1.0 g of catalyst in the apparatus described earlier. The catalyst was placed on top of the quartz wool positioned between the catalyst bed and the quartz chips used to reduce post-catalyst-bed dead volume. The catalyst sample was first pretreated in-situ at 680°C in an oxygen stream ($2.5\text{ cm}^3\cdot\text{min}^{-1}$) for a period of 16-20 hrs, then cooled to the required reaction temperature before steam and methane were introduced. A feed composition of $\text{CH}_4:\text{O}_2:\text{H}_2\text{O}=3:1:6.5$ moles and a total flow rate of $5.4\text{ cm}^3\cdot\text{min}^{-1}$ were employed.

The composition of the reactor effluent gas was analyzed by on-line gas chromatography.

Mg-Li oxide catalysts were prepared from their corresponding nitrates. A pre-ground and well homogenized mixture of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Mallinckrodt, AR grade flakes) and LiNO_3 (Aldrich, AR grade) was heated in air to near dryness. It was then cooled to room temperature and crushed to a powder-like form before being decomposed and calcined. The decomposition of this near dry powder-like material was carried out at a temperature of 250-550°C while calcination was conducted at 680°C for 14 hrs. The sample obtained was ground to a fine pale yellow powder before being tested. Two catalysts prepared by this method were designated as Li/MgO (A) and Li/MgO (B). In order to evaluate the effect of the preparation procedure on the catalyst's performance, different preparation regimes were used. Catalysts (C) and (D) were prepared by incipient wetness impregnation of MgO by an aqueous solution of lithium nitrate followed by calcination at 680°C. In all cases, a nominal catalyst composition of $\text{Mg}_2\text{Li}_1\text{O}_x$ was used. For comparison, a standard Li/MgO (Li: 4.1wt.% or equivalent to $\text{Mg}_4\text{Li}_1\text{O}_x$) catalyst (E) was used which had been obtained from Professor Lunsford's laboratory and which has been extensively investigated for its activity for the oxidative coupling of methane at high temperatures ($\geq 700^\circ\text{C}$).

In order to study the effects of variations of composition and preparation on the activity and selectivity of the Mg-Li-O catalysts, MgO, K/MgO, and various Li/MgO catalysts were employed. Results obtained are presented in Table 1.

MgO alone produced mainly carbon dioxide. Introduction of potassium into MgO did not improve its selectivity to hydrocarbons. In contrast, introducing lithium into MgO by means of co-decomposition of their corresponding nitrates followed by calcination at high temperature resulted in catalysts (e.g. Li/MgO(A) and Li/MgO(B)) of very high selectivity to hydrocarbons ($\geq 92\%$). However, Li/MgO catalysts prepared by incipient wetness impregnation of MgO with LiNO_3 aqueous (C, D) solution or by the Lunsford group's impregnation of MgO with Li_2CO_3 aqueous solution (E) showed only moderate increase in selectivity to hydrocarbons compared to the parent MgO catalyst. This clearly indicates that the procedure used for catalyst preparation plays a crucial role.

Table 1 Results of reaction of methane with oxygen in the presence of steam over various Mg-Li-O catalysts at 600°C ^a

Catalyst	Nominal Composition	Preparation Procedure	Conversion%			Selectivity %	
			CH ₄	Oxygen exp. cal.g		Hydrocarbons	CO _x ^b
Li/MgO (A)	Mg ₂ Li ₁ O _x	calcination ^c	10.1	70	20	96	4 (0)
Li/MgO (B)	Mg ₂ Li ₁ O _x	calcination	9.4	70	20	92	8 (0)
Li/MgO (C)	Mg ₂ Li ₁ O _x	incipient wetness ^d	9.2	70	60	30	70(0)
Li/MgO (D)	Mg ₂ Li ₁ O _x	incipient wetness ^e	8.7	70	60	24	76 (0)
Li/MgO (E)	Mg ₄ Li ₁ O _x	impregnation/ ^f	10	60	55	37	63 (1)
K/MgO (F)	Mg ₂ K ₁ O _x	calcination ^c	8.5	65	60	10	90 (3)
MgO (G)	MgO	calcination ^c	15.2	90	90	14	86 (1)

a, data taken from results obtained after 90 minutes of time on stream;

b, amount of carbon monoxide in brackets;

c, prepared from nitrates by calcination at 680°C;

d, incipient wetness of MgO prepared from Mg(NO₃)₂•6H₂O by LiNO₃ aqueous solution, then calcined at 680 °C;

e, incipient wetness of MgO (ultra-fine single crystal from Ube Industries Ltd.) by LiNO₃ aqueous solution, then calcined at 680°C;

f, prepared from Li₂CO₃ and MgO: dried at 140°C for 14 hrs, then 5°C•min⁻¹ to 500°C for 2 hrs, finally, 5°C•min⁻¹ to 700°C for 12 hrs;

g, estimation refers to text.

It appears that a MgO catalyst has higher activity (conversion of methane) than lithium-containing catalysts prepared from MgO. This is probably due to their difference in surface area. MgO has a much higher surface area than Li/MgO samples. The typical surface area of Li/MgO was around 1 m²•g⁻¹ while that of MgO was 15 m²•g⁻¹. The treatment of MgO with LiNO₃ solution had caused a significant decline in surface area; this may serve as an indication of incorporation of lithium into the MgO lattice and interaction between lithium and magnesium oxide.

The preparation of the catalyst is of great importance and is very sensitive to the procedure employed. It seems that preparations starting from nitrates produced catalysts of high activity and high selectivity to hydrocarbons, whereas incipient wetness impregnation of magnesium oxide with lithium nitrate solution or impregnation with lithium carbonate yielded catalysts of poor hydrocarbon selectivity. We also noticed that the presence of a small amount of residual water in the nitrate mixture before calcination may be necessary for high selectivity to hydrocarbons.

For an active and highly selective magnesium oxide based catalyst for oxydehydrogenation of methane, the presence of lithium is essential. Replacing lithium with potassium results in a significant decrease in selectivity to hydrocarbons. This is in agreement with Moffat's results obtained at high temperature (700-750°C) over M-P-O (where M= Li, Na, K, Rb, Cs, Be, Mg, Sr, Ba) oxide in the absence of steam. It was found that the selectivity to hydrocarbons shows a maximum for lithium. Further increase in R/C (ion radius/ion charge, Li⁺: 0.074 nm/charge; K⁺: 0.131 nm/charge) results in decline of selectivity to hydrocarbons.

Table 2 gives results of hydrocarbon distribution from a typical run at 600°C during ca. 3-4 hours. Conversion was steady as was selectivity at >94%. It is important to point out that blank runs without catalyst at the same conditions gave 0.5~1.0% conversion of methane to carbon dioxide. This amount of carbon dioxide would correspond to 5~10% carbon dioxide selectivity at a conversion level of 10% or what was observed in runs with a catalyst. A product ranging from C₂ to C₄ was formed. Amongst those hydrocarbon products, ethene and ethane are dominant.

Table 2 Product Distribution of Reaction of Methane with Oxygen in the Presence of Steam over Li/MgO(A) Catalyst at 600°C

Time on Steam/ min.	Selectivity to Hydrocarbons and Carbon Oxides %						CO ₂	Total hydrocarbons
	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄ +	CO		
65	33	49	4	5	2	0	7	93
145	35	51	4	4	2	0	4	96
225	28	63	2	3	1	0	3	97
300	3	8	0	0		2	87	13
380	2	7	0	0	0	2	88	12

The amount of hydrocarbon products generated decreased with the increase of their carbon number. Generally, the total amount of olefin products was less than that of paraffin products. After a period of 5 hours on stream, the formation of carbon dioxide predominated. The catalyst changed from one with very high selectivity to hydrocarbons in the oxidative coupling of methane to one which showed

predominantly oxidation activity leading to the formation of carbon dioxide. At the same time, the conversion of methane was considerably increased as the result of this product distribution shift.

Results obtained over Li/MgO (A) catalyst at three different temperatures are shown in Table 3. Conversion of methane and oxygen both increased with temperature. A reaction temperature of 600°C appears optimal for high selectivity to hydrocarbons. This seems to be somewhat different from previous results obtained with Ca₃NiK_{0.1} oxide catalyst, which showed that lower reaction temperature favors the coupling reaction while high reaction temperature favors oxidation of methane to carbon dioxide.

Table 3. Dependence of Product Distribution on Temperature ^{a,b}

Reaction Temperature/°C	Conversion %		Selectivity %	
	CH ₄	O ₂ exp. cal. ^d	Hydrocarbons	CO + CO ₂ ^c
550	5.5	35 35	15	85 (0)
600	10.1	70 20	96	4 (0)
650	13	90 70	45	55 (2)

a, catalyst: Li/MgO (A);

b, data taken after 90 minutes of time on stream;

c, amount of carbon monoxide in brackets;

d, estimation refers to text.

Table 4 and Table 5 contain results obtained with two different Li/MgO catalysts in the presence and absence of steam at two different temperatures. Data in Tables 4 and 5 show that the presence of steam is essential for high selectivity to hydrocarbons. In addition to this, the presence of steam also improved the catalyst's conversion activity, particularly at lower reaction temperatures. Another effect of steam is to increase the olefin to paraffin ratio. This is important because olefin products are more valuable than their paraffin counterparts. However, at higher reaction temperatures, the effect of steam is less significant in terms of both activity and selectivity. The effect of steam is far greater for catalysts prepared by nitrate co-decomposition (e.g. catalyst Li/MgO (A)) than for those prepared by incipient wetness (e.g. catalyst (C)) and impregnation with carbonate (e.g. catalyst (E)).

Based on hydrocarbon product distribution data obtained from GC analyses and the relationship between hydrocarbon formation and oxygen consumption (2

$\text{CH}_4 + 1/2 \text{O}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O}$; $2 \text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + 2 \text{H}_2\text{O}$; $\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$), the amounts of oxygen required to their formation were estimated and

Table 4 Effect of steam on reaction of methane with oxygen over Li/MgO (A)
Catalyst^a

Temperature /°C	Steam	Conversion%			Selectivity %		
		CH ₄	O ₂		CO _x ^b	Hydrocarbons	C ₂ '/C ₂ ^o
			exp.	cal. ^d			
600	yes	10.1	70	20	4 (0)	96	0.6
600	no	8.6	75	70	91 (2)	9	0.3
650	yes	13.5	90	70	55 (3)	45	0.8
650	no	12.0	90	80	68 (2)	32	0.2

- a, Methane: 1.5 cm³•min⁻¹; O₂: 0.5 cm³•min⁻¹; H₂O: 3.3 cm³•min⁻¹;
b, amount of carbon monoxide in brackets;
c, catalyst pretreated at 700 °C in oxygen;
d, estimation refers to text.

Table 5 Effect of steam on reaction of methane with oxygen over Li/MgO (E)
Catalyst^a

Temperature /°C	Steam	Conversion%			Selectivity %		
		CH ₄	O ₂		CO _x ^b	Hydrocarbons	C ₂ '/C ₂ ^o
			exp.	cal. ^c			
600	yes	10.0	60	55	63 (1)	37	0.7
600	no	8.0	65	58	69 (1)	31	0.6
700	yes	11.7	65	55	70 (8)	30	1.5
700	no	11.2	68	58	74 (7)	26	0.9

- a, Methane: 1.5 cm³•min⁻¹; O₂: 0.5 cm³•min⁻¹; H₂O: 3.3 cm³•min⁻¹;
b, amount of carbon monoxide in brackets;
c, estimation refers to text.

included in Table 1 and Tables 3-5. All the data (cf. Table 1, and Tables 3-5) show that better oxygen and carbon balance were obtained with catalysts of poor hydrocarbon selectivity while catalysts of high hydrocarbon selectivity show an appreciable degree of mismatch between the amount of methane converted and the amount of oxygen consumed. This discrepancy may be attributed to the deposition of carbonaceous material on the catalysts although no quantitative data have been obtained. The formation of these carbon-rich and hydrogen-deficient species required oxygen,

leading to the formation of water. Therefore, there were larger amount of oxygen reacted than were required to convert that amount of methane into hydrocarbon products. This is in agreement with the lack of carbon balance in the first one to two hours of reaction observed previously. This question needs to be addressed further in the future work. The amount of water formed from sources other than those given in the beginning of this section should be estimated by measuring the total amounts of water formed in the reaction. However, due to the much larger amount of water (in the form of steam) introduced into the system relative to the amount of water formed, there were practical difficulties associated with this. Thus, quantitative data on water formation are not available.

Due to the fact that the present studies were carried out at lower temperature (600°C) compared to the widely used high temperature ($\geq 700^\circ\text{C}$), we feel confident that the reaction is catalytic in nature. The active sites responsible for this selective coupling of methane are believed to be those O^- species formed on the catalyst surface. This can be inferred from the work of Freund et al. and others. By using charge distribution analysis technique, they have shown that O^- is the charge carrier of CaO , $\text{Na}_2\text{O}/\text{CaO}$, $\text{La}_2\text{O}_3/\text{CaO}$, MgO , Li/MgO , and other oxide catalysts, and they believed that this is true for most oxide catalysts used for the oxidative coupling of methane. It is these O^- species which are responsible for the selective oxidative coupling of methane. In the case of Li/MgO , the O^- species are mainly formed by replacing of Mg^{2+} cations by Li^+ cations. These species exist in the form of peroxy anion O_2^{2-} at temperature below 550-600°C. The later thermally decomposes into O^- at temperatures above 550-600°C. Thus, in order to initiate oxidative coupling of methane, it is necessary to carry out the reaction at temperatures high enough to generate O^- from those dormant peroxy anions O_2^{2-} because peroxy anion itself is not able to facilitate the selective oxidative coupling of methane. This may explain the observed lower selectivity to hydrocarbons at 550°C (cf. Table 3). Coupling activities observed at temperature 550-600 °C in the present work is in excellent agreement with the observation that highly mobile charge carriers (i.e. O^-) were observed above a threshold temperature of about 550-600°C. Furthermore, the presence of steam may enhance the decomposition of peroxy anion O_2^{2-} into O^- species and to the formation of surface OH^- groups which then undergo homolytic splitting to form O_2^{2-} ; these dissociate above 550°C according ($\text{O}_2^{2-} \rightarrow \text{O}^- + \text{O}^-$) whereby one O^- remains bound to the vacancy while the other O^- becomes unbound as suggested by Freund et al [9, 11]. Therefore, the presence of steam is necessary to produce O^- at temperature around 550-600 °C and to maintain the supply of O^- species. Steam will also desorb any oxygen molecules on the catalyst surface which tend to produce carbon dioxide. However, at high temperature, the decomposition of O_2^{2-} can proceed without the assistance of steam, thus the presence of steam may not be required. In addition, it is also probable that high temperature may not favor the formation of surface OH^- groups.

The catalysts studied suffered significant deactivation in terms of selectivity to hydrocarbons under the conditions used. After deactivation, the catalyst

performance changed from very high selectivity to hydrocarbons to almost exclusively to the formation of carbon dioxide. Preliminary results obtained by X-ray diffraction of the fresh and used catalysts showed formation of Li_2CO_3 in the used catalyst samples. However, the high selectivity to hydrocarbons observed in this study cannot be attributed to the formation of Li_2CO_3 because the level of Li_2CO_3 was not substantial in the used catalyst samples. The investigation of causes for catalyst deactivation and its prevention are under way.

In order to investigate the potential effect of a transition metal oxide on the performance of an active Li-Mg-O_x catalyst a lithium magnesium nickel oxide catalyst was prepared by physically mixing of lithium-magnesium-oxide derived from nitrate and nickel oxide so that the nominal composition of the resulting catalyst was $\text{Mg}_3\text{NiLi}_{1.5}$. The data in Table 6 shows that the addition of nickel oxide into an active lithium magnesium oxide catalyst did not enhance the performance of the catalyst in terms of both activity and selectivity to higher hydrocarbons. By inference this suggests that the presence of a transition metal cation in the lithium magnesium oxide catalyst is not essential and that in this respect, lithium magnesium oxide is different from the calcium nickel potassium oxide which requires the presence of a transition metal ion.

Table 6 The Effect of adding NiO into Li/MgO catalyst for the oxidative coupling of methane

TOS/min	Conv %		Sel. %/ HC		Sel.%/CO ₂	
	Mg-LiO _x	MgLi-NiO _x	Mg-LiO _x	MgLi-NiO _x	Li-MgO _x	LiMg-NiO _x
40	8.8	0.4	92.9	61.0	7.1	39.0
79	12.5	0.7	93.3	84.9	6.7	15.1
118	13.3	1.2	95.8	94.0	4.2	6.0
157	11.1	9.6	95.4	7.0	4.6	93.0
196	10.8	7.9	94.9	12.7	5.1	87.3
235	8.9	12.5	93.6	6.3	6.4	93.7
274	3.1	11.0	77.4	5.9	22.6	94.1
313	6.9	7.3	21.8	14.1	78.2	85.9
352	7.4	11.6	20.3	4.3	79.7	95.7
391	6.9	-	22.7	-	77.3	-

Li/MgONiO was prepared by physically mixing Li/MgO and NiO so that the nominal composition of the resulting catalyst = $\text{Mg}_3\text{NiLi}_{1.5}$

ii) *Ca-Ni-K Oxide Catalysts*

A study was undertaken to determine the optimum temperature range for the catalyst activation treatment. The results are shown in Table 7, which forms

TABLE 7

Ca₃NiK_{0.1} CATALYSTCH₄:O₂:H₂O = 3:1:6 moles; 600 °C; Flowrate: 4mmole CH₄/g cat/hr

Catalyst activated in O ₂ for 18 hrs at	Conversion %	Selectivity to C ₂ + Hydrocarbons, %	Selectivity to CO _x %
600 °C	24	0.2	99.8
650 °C	15	75	25
680 °C	10	94	6
700 °C	9	89	11
750 °C	8	69	31

the basis of a continuation-in-part patent application. The preferred range is 650-700°C.

Fresh and deactivated catalysts were characterized by x-ray diffraction. The deactivated catalyst showed a major increase in CaCO₃ content of the catalyst. Regeneration of the catalyst in oxygen at 680°C resulted in the removal of almost 2/3 of the carbonate and regeneration with oxygen and steam at 680°C gave almost complete carbonate removal as shown below:

<u>Sample</u>	<u>CaCO₃/CaO_x Ratio</u>
Fresh catalyst	0.05
After 8 hr. operation	3.68
After operation and regeneration in O ₂ at 680°C	1.41
After operation and regeneration in O ₂ + steam at 680°C	0.02

Work is underway to determine the period of carbonate formation and the steady state concentration at 600°C.

The potential effect of particle size on the performance of a Ca₃Ni₁K_{0.1}O_x catalyst was investigated. The results are shown in Figure 2. It appears that surface area is almost independent of particle size. Hydrocarbon selectivity is high below 0.2 mm particle size, as is conversion. Above 0.2 mm selectivity to higher hydrocarbons decreases and CO₂ selectivity increases correspondingly.

c) *Synthesis and Characterization of Catalysts*

During this quarter, several instrumental techniques were utilized to study changes in catalysts in their initial states and after they had been used in the catalysis process. For this purpose, two samples (9206-0 and 9206-2) underwent parallel analyses using infrared and x-ray photoelectron spectroscopy and powdered x-ray diffraction. The two samples consisted of (1) a freshly prepared Ca₃Ni₁K_{0.1}O_x catalyst which had not been calcined or oxygen treated (9206-0) and (2) the same catalyst after oxygen treatment at 680°C and operation at 600°C for 6 hours while passing CH₄:O₂:H₂O over it in a 3:1:6 ratio (9206-2).

Several differences in the samples were noticed. First, several bands in the Fourier transform infrared spectra were different, both with respect to line intensities and shapes. Sample 9206-2, for example, exhibits a much stronger and more complex vibrational band structure at 1423 cm⁻¹ than the corresponding band at 1416 cm⁻¹ for the 9206-0 sample. Internal ratios for different lines in each spectrum also differ for the two samples.

X-ray diffraction data showed species that were consistent with all those seen for other samples studied in the Ca-Ni-K-O system. The species included Ca(OH)₂,

CaO, KO₂, and NiO. Additionally, in the 2906-2 sample, diffraction peaks were present for the calcite form of CaCO₃.

X-ray photoelectron data showed Ca 2p, O 1s, Ni 2p lines and the associated satellite structure (in the case of nickel) to be consistent with the above mentioned species. The C 1s photoline for the 2906-2 sample showed a carbonate peak that was consistent with the x-ray diffraction data mentioned above. Additionally, the main nickel 2p_{3/2,1/2} photoelectron lines showed considerable differences between the two samples. The nickel lines for the 9206-0 sample showed much asymmetry and more complex band structure, indicating the possibility of more than one nickel species on the surface. While effects such as charging could be used to explain this, no such effects were noted for the other sample which showed about the same spectral position for the "adventitious" carbon. Smaller amounts of the carbonate species were also detected on the 2906-0 sample.

With respect to quantitative differences of the elements on the surfaces of the two samples, in going from Sample 9206-0 to 9206-2, nickel dropped by about half (4.90% vs. 3.30%). Calcium dropped slightly (17.7% vs. 15.0%), while potassium increased from 1.74% to 2.75%. Carbon and oxygen remained approximately constant, comprising approximately 20% and 55-50%, respectively. These compositions have been normalized to 100%.

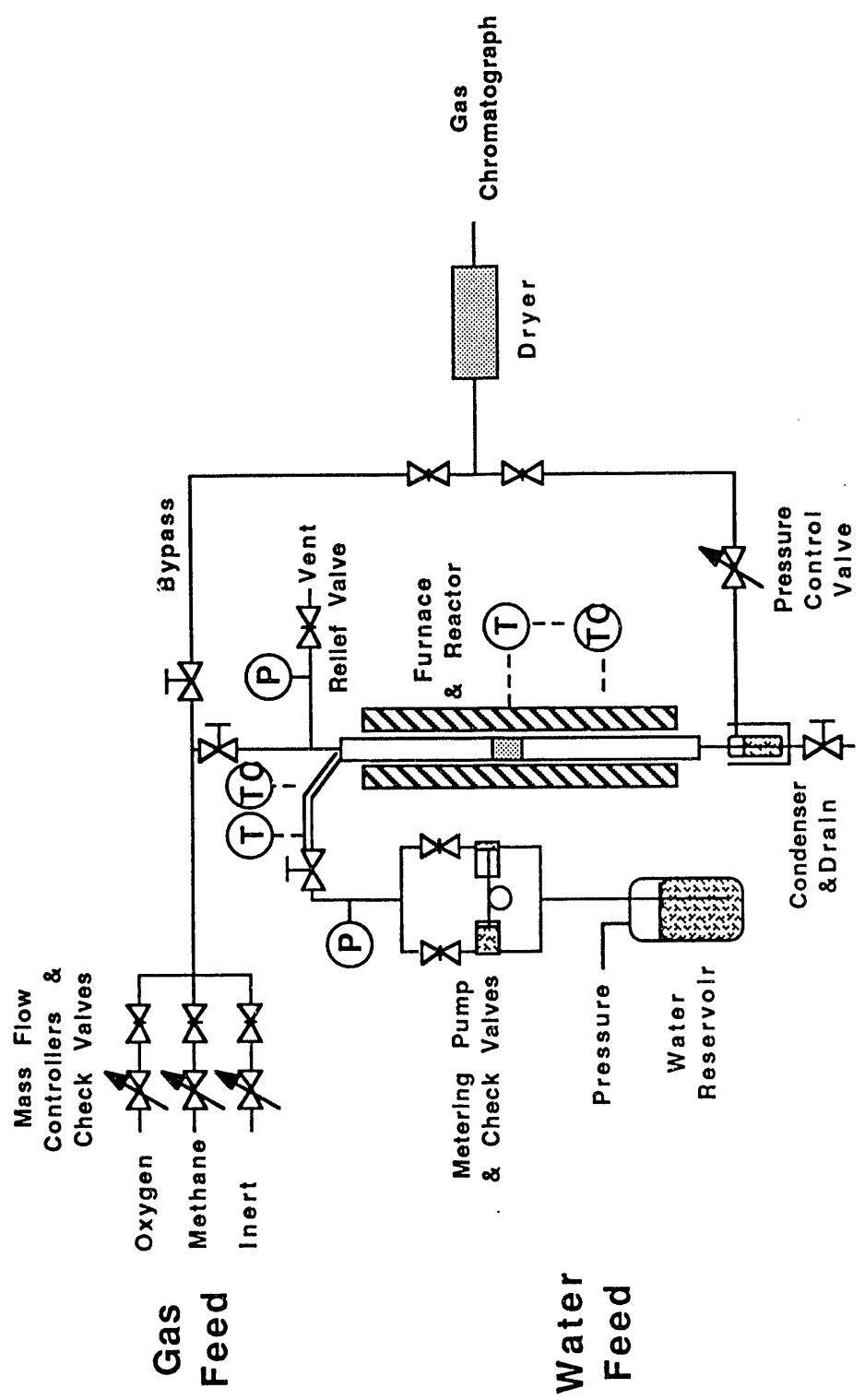


Figure 1

CaNiK performance vs particle size 3.0:1:0.1, Physical mixture, 116min

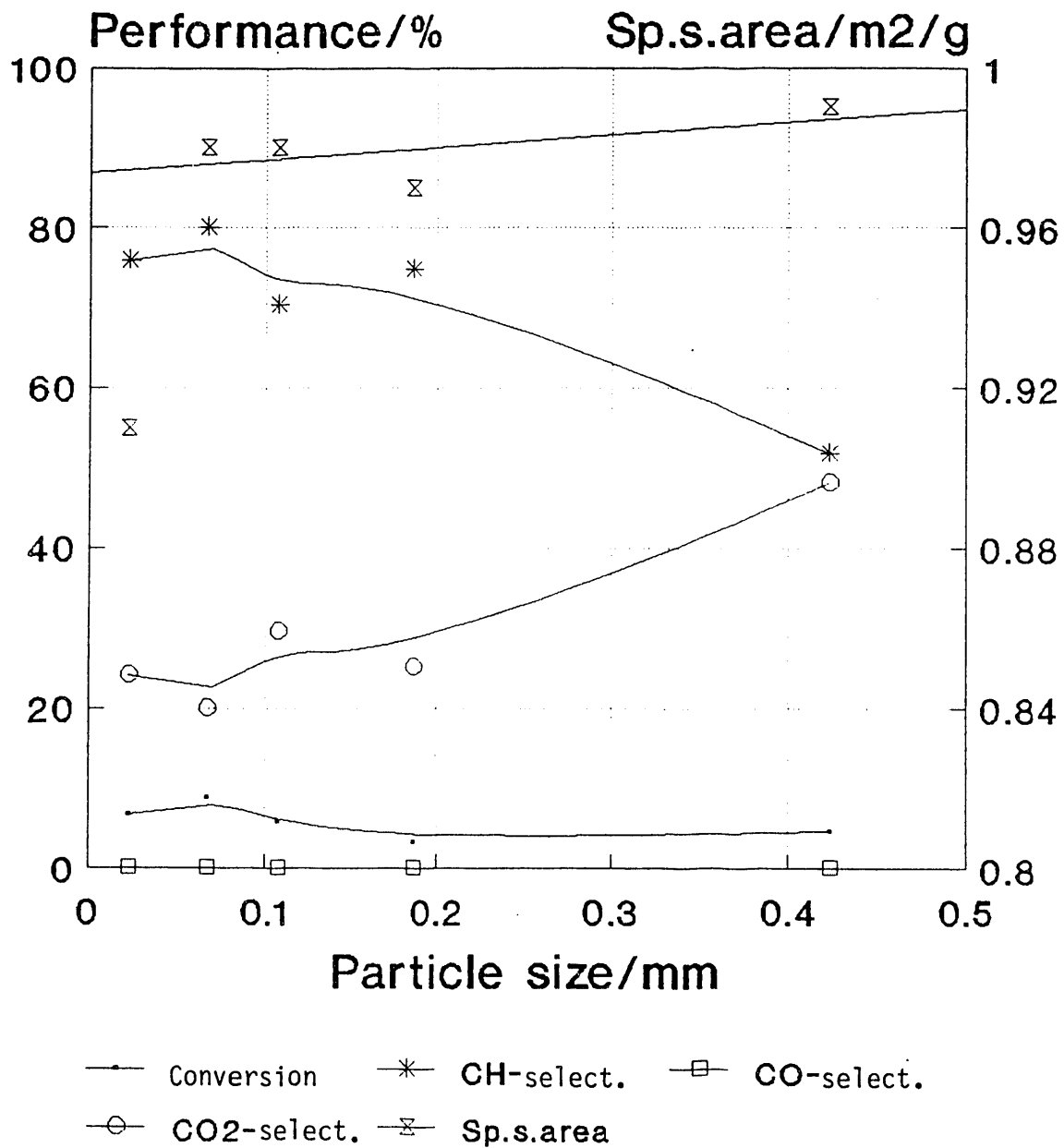


Figure 2

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