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QUARTERLY REPORT

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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 1993

Task 1: Work on catalytic steam gasification with chars and coals will be extended from atmospheric to elevated pressures using the newly built pressure unit. The novel finding that coking of petroleum in the presence of small amounts of caustic greatly improves the gasification rates and characteristics of the coke will be extended to chars. The chars will be prepared by charring coals in the presence of minor amounts of caustic and the resulting chars will be steam gasified in the absence and presence of catalysts.

Task 2: In the oxidative coupling of methane over ternary catalysts, a large number of factors remain poorly understood and must be investigated to improve results and move them into the commercially interesting area. Emphasis will be placed on low temperature coupling and on the oxidative production of syngas from methane at low temperature. Work on the CRADA between LBL and Orion ACT will continue and will be expanded to include methane coupling to higher hydrocarbons in a membrane reactor. Isotope studies will be undertaken to better understand the nature of the active catalyst sites.

Task 3: Experimental work will continue on the synthesis of the mixed catalyst, and they will be characterized by a number of techniques, including elemental analyses, x-ray diffraction, and surface area determination. Scanning electron microscopy will be used to monitor the variations of the surface morphology as a function of the preparative route. X-ray photoelectron, Auger, Raman and infrared spectroscopy will be used to study chemical and bonding aspects of the catalysts.

II. Highlights

a) Catalytic Steam Gasification of Coals and Cokes

- Petroleum cokes have somewhat lower gasification rates than bituminous coal chars.
- Both coal chars and petroleum cokes show greatly improved catalytic gasification rates when they are prepared in the presence of caustic.
- A paper on catalytic steam gasification of chars and cokes has been submitted for publication (Appendix a).

b) Oxidative Methane Coupling

- Oxidative coupling of methane to higher hydrocarbons has been investigated over lithium-magnesium oxide catalysts at $\sim 600^\circ\text{C}$ and low space velocity. The presence of steam is essential to obtain C_2^+ hydrocarbons. In the absence of steam, oxidation to syngas and CO_2 predominates. A publication has been written and submitted to JOURNAL OF CATALYSIS (Appendix b).
- In this quarter, efforts have been made to understand the nature of active surface sites on Ca-Ni-K and Mg-Li oxide catalysts and the role played by water in the oxidative coupling of methane because there is not much information about how and why these catalysts work. The major techniques used to probe active oxygen species on catalyst surfaces include temperature programmed isotopic exchange (TPIE) and temperature programmed desorption (TPD). TPIE was used to study the exchange between lattice and gas phase oxygen and TPD was used to characterize the interaction between probe molecules (e.g., H_2O , CO_2) and catalyst surface.
- Two types of active surface sites were found: one responsible for single exchange between lattice oxygen and gas phase oxygen; the second being responsible for multiple exchange between lattice oxygen and gas phase oxygen. The amount of lattice oxygen exchangeable by gas phase oxygen depends on both the nature of the catalyst and exchange temperature. At temperatures $\leq 750^\circ\text{C}$, Mg-Li oxide has the highest exchange capacity ($>10\%$). Ca-Ni-K (A) and Ca-Ni-K (B) have comparable amounts ($\sim 5\%$) of lattice oxygen exchangeable by gas phase oxygen.
- A program was started to explore oxidative coupling of methane in a membrane reactor, using a perovskite membrane.

c) Synthesis and Characterization of Catalysts

- Fourier transform infrared spectroscopy has identified $-\text{CH}_2-$ groups in char samples which have been partially gasified in the presence of K-Ca oxide catalysts.

IV. Progress of Studies

a) Catalytic Steam Gasification of Coals and Cokes

A paper *Factors Affecting the Reactivity of Chars and Cokes During Low Temperature 640°C Steam Gasification* has been written and submitted to ENERGY AND FUELS for publication. A copy is attached in Appendix *a* of this report. While most of the information in the paper has been previously reported, the data in Figures 2, 3, 4, and 5 of the paper (Appendix *a*) give a new comparison of the gasification characteristics of chars and petroleum cokes and show that in general, cokes have slower gasification rates than chars. It is also demonstrated that incorporation of caustic into the charring, resp. coking procedure greatly increases the gasification rates.

Experimental work during the first quarter of FY 1993 has been concentrated on catalytic gasification of subbituminous chars in the presence and absence of NaOH during the charring process. Results are insufficiently complete at this time to warrant inclusion in this report.

Samples from the study of the effects of pyrolysis conditions on char and coke gasification were submitted to Dale Perry in the Earth Sciences Division for compositional and structural evaluation. Preliminary infrared results show significant differences in structure at different stages of pyrolysis and gasification. Detailed analysis of the complete results is in progress.

b) Oxidative Methane Coupling

The oxidative coupling of methane to C₂ and higher hydrocarbons over magnesium-lithium oxide catalysts has been investigated at relatively low temperatures (> 600°C) in the presence and absence of steam and at low space velocity. The presence of steam is essential to the formation of coupling products, while in the absence of steam partial oxidation to syn-gas and CO₂ formation become dominant. At optimum conditions ~30% selectivity to C₂⁺ hydrocarbons was obtained at 18-22% conversion. A paper has been prepared and submitted for publication in THE JOURNAL OF CATALYSIS. This paper is appended in Appendix *b* of this report.

Temperature programmed isotope exchange and temperature programmed desorption studies were undertaken for the oxidative coupling of methane over Ca-Ni-K oxide and Mg-Ni oxide catalysts.

We distinguished two types of surface active sites: one responsible for single exchange between lattice oxygen and gas phase oxygen; and the second being responsible for multiple exchange between lattice oxygen and gas phase oxygen;

The amount of lattice oxygen exchangeable by gas phase oxygen depends on both the nature of the catalyst and exchange temperature. At temperatures $\leq 750^{\circ}\text{C}$, Mg-Li oxide has the highest exchange capacity ($>10\%$). Ca-Ni-K (A) and Ca-Ni-K (B) have comparable amount ($\sim 5\%$) of lattice oxygen exchangeable by gas phase oxygen.

For Li/MgO catalyst, there are at least two kinds of surface sites which are responsible for the single exchange reactions occurring at 550°C and 660°C respectively; there is probably only one type of active site which is responsible for the multiple exchange reaction at 510°C . The minimum temperature required for the isotopic exchange is 300°C . However, the amount of isotopic exchange below 400°C is negligible. Active sites responsible for multiple exchange reactions represent $\sim 20\%$ of the total number of active sites.

For one type of Ca-Ni-K catalyst, there are three types of surface sites which are responsible for the single exchange reactions incurred at 430°C , 580°C , and $\geq 750^{\circ}\text{C}$. Those sites which are responsible for the exchange reaction at 430°C are far less important than those responsible for the exchange required at higher temperature (580°C , $\geq 750^{\circ}\text{C}$). There seem to be three types of surface sites which are responsible for multiple exchange reactions at 450°C , 520°C and $\geq 720^{\circ}\text{C}$. The sites responsible for the exchange reaction at 520°C are dominant. Among these active surface sites for oxygen exchange reactions, $\sim 7\%$ are responsible for multiple exchange reaction.

For another type of Ca-Ni-K catalyst, there are two types of active sites responsible for single exchange reactions at 480°C and $\geq 750^{\circ}\text{C}$. These sites for high temperature exchange reaction are more significant than the ones for low temperature. Two types of active sites responsible for double exchange are found in this catalyst. They are responsible for the exchange at 440°C and $\geq 740^{\circ}\text{C}$. The multiple exchange sites represent only a very small fraction ($<3\%$) of the sites responsible for isotopic exchanges.

From the isotopic exchange data in Table 1, we calculated that the amount of lattice oxygen exchanged by gas phase oxygen is equivalent to approximately 20 atomic oxygen layers by assuming that each oxygen atom occupies $12.5\text{\AA}^2$ or that there are 10^{19} oxygen atoms per cm^2 .

Table 1 Results of Surface Analysis and Isotopic Exchange

Catalyst	Composition (atomic ratio)		BET Surface Area	O ₂ exchanged ^a
	nominal	XPS	m ² •g ⁻¹	%
Li-Mg oxide	1:2	1:3	0.7	>10
Ca-Ni-K oxide (A) ^b	31:10:1	15:5:1	1.8	> 4
Ca-Ni-K oxide (B) ^c	29:9:1	13:4:1	2.1	>5

- a. amount of lattice oxygen exchanged by gas phase oxygen at temperature $\leq 750^{\circ}\text{C}$ during the temperature programmed exchange experiment;
- b. prepared by decomposition of a mixture of $\text{Ca}(\text{NO}_3)_2$, and $\text{Ni}(\text{NO}_3)_2$, and KNO_3 at 700°C ;
- c. a physical mixture of CaO , NiO , and KNO_3 ;

Membrane Reactor

A project was begun in which oxidative coupling will take place in a reactor which contains a proton-conducting perovskite oxide membrane. This reaction has been successfully demonstrated with a surface reactivity of $250\mu\text{mol}/\text{m}^2 \cdot \text{s}$ with 100% selectivity to hydrocarbons at 800°C . The reaction proceeds as follows:

1. H Abstraction from CH₄ by Surface O⁻.

2. Proton (H⁺/OH⁻) Diffusion Across Membrane.

$$\bullet \frac{1}{A} \frac{d[\text{H}^+]}{dt} = D_{\text{H}^+} \frac{[\text{H}^+]_{\text{CH}_4} - [\text{H}^+]_{\text{O}_2}}{\Delta x}$$

3. O⁻ Regeneration by O₂.

4. Hole (h⁺/O⁻) Diffusion Across Membrane.

$$\bullet \frac{1}{A} \frac{d[h^+]}{dt} = D_{h^+} \frac{[h^+]_{\text{O}_2} - [h^+]_{\text{CH}_4}}{\Delta x}$$

Reactivity was limited by the large resistance to proton and hole fluxes across the ~2 mm thick membrane. Membranes with thicknesses of ~1 μm, made by thin film deposition (e.g., sol-gel deposition¹), will have reduced resistances to ionic fluxes. Chemicals for the production of SrCeO₃⁻ and SrZrO₃⁻ based membranes have arrived, and membranes will be made presently. Construction of the membrane-supporting apparatus is in progress. Issues of importance will be membrane quality (defect density) and stability to operating conditions. Results of the reactivity of these membranes will be forthcoming in the following quarter.

c) *Synthesis and Characterization of Catalysts*

Fourier transform infrared spectroscopy was performed on a number of carbonaceous coal/char samples. The samples were ground to a fine powder, mixed with KBr powder, and compressed into pellets for the transmission measurement. Most samples show a number of characteristic absorption features, some of which have been identified and some which have not. The group -CH₂- is identified in samples by absorption at 2920 and 2850 cm⁻¹. Many of the samples exhibit absorption near 1600 and 1030 cm⁻¹ which is attributed to C=C.

The carbonate ion CO₃⁻² is identified by absorption at 1450 and 857 cm⁻¹. Also present in a number of samples is a doublet at 435 and 470 which is believed to be due to the presence of monobranched alkanes. Variable absorption near 5400 cm⁻¹ is due to OH⁻. Several additional absorption features have not yet been identified.

¹Kueper, et. al., *Solid State Ionics*, 52 (1992), 2945.

Factors Affecting the Reactivity of Chars and Cokes During Low Temperature (640°C) Steam Gasification

by

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Abstract

Coal chars and petroleum cokes were prepared by low temperature pyrolysis, both in the absence and presence of NaOH. The solids obtained were gasified with steam at 640°C, either as-prepared or after impregnation with a K-Ca oxide catalyst. The uncatalyzed steam gasification rate increases with NaOH loading, and slows with increasing time on stream due to the slow vaporization of sodium and the decrease in contact time as the char/coke is consumed. The K-Ca oxide catalyst accelerates gasification, especially for NaOH-containing solids. Pyrolysis temperature and gasification pressure had minor effects. Gasification reactivity depends on the source of carbon, which is related to the structure and hydrophilicity of the fixed carbon.

Introduction

Useful chemicals (*e.g.*, hydrocarbon gases, tar chemicals) are obtained from coals and petroleum resids during pyrolysis [1,2], leaving solid carbon (chars and cokes, respectively) as significant by-products. Solid disposal problems can be reduced by gasifying the carbon with steam, oxygen, or CO₂ to produce reactive gas mixtures, such as fuel or synthesis gases [1]. Carbon gasification, particularly with steam, has been studied extensively [*e.g.*, 3-11], yielding a great deal of empirical data and insight into the reactions involved.

The carbon source and the pyrolysis conditions strongly affect the steam gasification reactivity [5-7]. The carbon source determines the initial arrangement of fixed carbon and volatile matter, while the pyrolysis temperature determines the extent to which those structures rearrange [1]. In addition, the presence of NaOH during coal pyrolysis has been shown to affect the surface and plasticity properties of the resultant chars [12], which are associated with the structures on the coal surface. All of these factors should have significant effects on the steam gasification reactivity.

Catalysts, particularly alkali metal and binary oxides, have been added to the carbon to improve its reactivity [3-11]. A K-Ca oxide catalyst was found to greatly improve the solid reactivity, allowing relatively low temperature ($< 700^{\circ}\text{C}$) steam gasification of graphite and chars with significant resistance to poisoning by sulfur [5]. NaOH is also an effective catalyst [9].

Fossil fuel processing generates many caustic waste streams which may be added to the coal or resid in place of NaOH. During gasification, the sulfur in these streams and in the char/coke reacts to form H_2S [14,15], which is recovered in the gaseous products, and can be converted to elemental sulfur. Waste disposal is thereby reduced with the recovery of useable products.

With the K-Ca oxide catalyst and relatively low temperatures, hydrogen is the primary product of gasification, with CO_2 being the main co-product [5,8]. Hydrogen is used mostly in high-pressure hydroprocessing reactions, it is desirable to produce the H_2 by gasification at elevated pressures. In one study, total pressures up to 28 atm were shown to have no effect on the steam gasification rate of a particular coal char [13]. This result has yet to be extended to other systems.

The present study investigates the reactivity of carbon for steam gasification as affected by: the presence of NaOH during pyrolysis; the pyrolysis temperature; the carbon source (bituminous or subbituminous coal or petroleum resid); the substitution of NaHS for NaOH; and the gasification pressure.

Experimental

Char/Coke Preparation

Argonne Premium coals (Illinois #6 high volatile bituminous and Wyoming subbituminous [16]) were heated at 500°C or 640°C for 2 h to produce the chars. Lower char yields were obtained at the higher temperature, due to the removal of residual volatile matter. The caustic-containing chars were obtained by adding a NaOH solution (10 or 20 wt% NaOH, 8.5% of the coal weight) to the coals prior to heating. Swelling of the Illinois coal during heating was eliminated by NaOH addition, consistent with the results of a previous study [12].

Cokes (from Mobil R&D Corp., nominal composition range, 100 C atom basis, $C_{100}H_{43.51}N_{0.08}O_{0.3-2.0}S_{0.2-2.7}$ trace Ni, V, and Fe [17]) were produced by heating petroleum residua (typical composition, 100 C atom basis, $C_{100}H_{138}N_{0.8}O_{0.4}S_{2.4}$, [15]) at temperatures up to 500°C. Caustic-containing cokes were obtained by heating of the same parent resids after mixing with caustic solutions (containing NaOH or NaHS; similar Na loading as for chars).

Steam Gasification

The steam gasification apparatus is illustrated in Fig. 1. The reactor (1) is pressurized with nitrogen to the operating pressure, which is maintained by a back pressure regulator (2, Tescom). Nitrogen flow is controlled by a thermal mass flow controller (3, Porter Instruments), and the reactor is heated in a split tube furnace (4, Lindberg). Water is pumped from a reservoir (5) by a valveless piston pump (6, IVEK) into a length of heated tubing (7, 250°C) to generate steam which then flows with the nitrogen over the heated char, producing gaseous products. Unreacted water is removed from the product stream in a condenser (8, 0°C) prior to gas analysis by GC/TCD (9).

The char/coke (0.5 g) is reacted with 3 mmol/min steam (corresponding to 0.055 cc/min liquid flow rate) in 2.0 cc/min of flowing nitrogen at 640°C. For the catalyzed gasification reaction, a K-Ca catalyst was added to the solid prior to gasification, by impregnation with an equimolar solution of KNO_3 and $Ca(NO_3)_2 \cdot 4H_2O$, and drying at 200°C for 10 h. Catalyst loading was K:Ca:C = 1:1:100 assuming 80 wt% C in the solid.

The main products of gasification are H_2 and CO_2 . Conversion calculations were based on the cumulative production of hydrogen, because calculations of conversion based on CO_2 production were impossible due to the solubility of CO_2 in the condensate.

Results

Presence of NaOH during pyrolysis and pyrolysis temperature

The effects of NaOH loading and pyrolysis temperature on the rate of steam gasification of Illinois #6 bituminous coal chars are shown in Fig. 2, which presents the carbon conversion as a function of time (Fig. 2a) and the hydrogen production rate as a function of carbon conversion (Fig. 2b). The Illinois #6 high volatile bituminous coal was charred without any NaOH (closed symbols) and with the addition of 8.5 wt% loading of 10% NaOH (crossed symbols) or 20% NaOH (open symbols). Pyrolysis temperatures were 500°C (circles) and 640°C (squares). Gasification was at 640°C. It is apparent that charring with increasing NaOH loadings increases the initial conversion rate for the chars produced at 500°C. Increasing pyrolysis temperature without any NaOH decreases the steam gasification rate initially, but not at higher conversions (> 5%). When using NaOH, pyrolysis at 640°C gave chars that were much less reactive through 10% conversion than the low temperature chars.

Figure 3 shows how charring with NaOH and addition of the K-Ca oxide catalyst affect steam gasification of Illinois #6 chars. The carbon conversions (Fig. 3a) and the hydrogen production rates (Fig. 3b) are compared for chars that were obtained without (circles) and with (squares) 8.5 wt% loading of 20% NaOH for uncatalyzed (closed symbols) and catalyzed (1% K-Ca catalyst - open symbols) steam gasification. It is evident that, for the NaOH-free char, gasification with the catalyst is much faster. For the NaOH-containing char, the enhancement of gasification due to the addition of the catalyst is even greater, and the gasification rate does not decrease significantly through 60% conversion.

Carbon Source

a. NaOH absent during pyrolysis

Figure 4 (Fig. 4a - conversion vs. time, Fig. 4b - H_2 production rate vs. conversion) compares the K-Ca oxide catalyzed steam gasification reactivity of solids obtained by pyrolysis in the absence of NaOH of various carbon sources: petroleum coke from Statfjord residuum (closed circles), petroleum coke from Torrance residuum (closed squares) Illinois #6 bituminous coal char (open circles), and Wyoming subbituminous coal char (open squares). The petroleum cokes show similar reactivity to each other, attaining 5-10% conversion after 250 min, but are much less reactive than the chars. The subbituminous char reacts the fastest, with almost complete conversion, and the bituminous char is also somewhat reactive, with 20% conversion after 200 min.

b. NaOH present during pyrolysis

Figure 5 (Fig. 5a - conversion vs. time, Fig. 5b - H_2 production rate vs. conversion) compares the K-Ca oxide catalyzed steam gasification reactivity of solids obtained by pyrolysis of various carbon sources (symbols - same as for Fig. 4) in the presence of NaOH. Comparing Fig. 5 with Fig. 4 reveals that, in all cases, pyrolysis with NaOH enhances the reactivity of the carbon solid. Charring of the subbituminous coal with NaOH had a modest effect, such that 100% conversion is obtained after 300 min of gasification. The effect of charring the bituminous coal with NaOH doubled the catalyzed reactivity, as previously described. The effect of caustic modification, however, was most dramatic for the petroleum cokes. The NaOH-containing Statfjord coke showed reactivity similar to the NaOH-containing subbituminous char, while the reactivity of the corresponding Torrance coke was enhanced almost to that of NaOH-containing bituminous char.

c. Substitution of NaHS for NaOH

Figure 6 is a graph of conversion vs. time for the steam gasification of petroleum coke obtained from the Maya residuum, showing the effect of coking with the refinery-derived caustic waste stream (23 wt% NaHS) on the gasification reaction. Gasification without NaHS or K-Ca oxide catalyst (not shown) leads to negligible reaction on the timescale of this figure. Comparing the gasification of the NaHS-free coke with the K-Ca catalyst (open squares) and of the NaHS-containing coke without

(closed squares) and with (asterisks) the K-Ca catalyst shows that the enhancement of steam gasification obtained by coking with NaHS is similar to that obtained by coking with NaOH.

Gasification Pressure

In general, pressure does not appear to have an effect on gasification, except in one case. Gasification of the NaOH-free char (not shown) was not sensitive to pressure, in agreement with a previous study which showed no effect of pressure (up to 28 atm) on gasification [13]. Figure 7 shows the reactivity of the 500°C pyrolysis temperature chars with 8.5 wt% loading of 20% NaOH, comparing the conversions (Fig. 7a) and H₂ production rates (Fig. 7b) during steam gasification at 1 atm (closed symbols) and 7.8 atm (100 psig - open symbols). The catalyzed gasification (squares) shows no effect of pressure. The uncatalyzed gasification (circles) shows an enhancing effect of pressure, such that the reaction does not slow down, even after 40% conversion.

Discussion

Pyrolysis of the organic volatile matter in coal generally begins near 350°C and is complete around 700°C [1,18]. The gasification reactivity of the 500°C Illinois #6 coal char has an initial burst of high reactivity associated with residual volatile matter [6], and then levels off at a lower activity associated with the fixed carbon. Gasification of the 640°C char shows no initial burst, but after a short induction period has the same reactivity as the 500°C char. The lower initial rate occurs because charring at 640°C removes most of the remaining volatile matter [18]. The similar rates for the two chars at conversions above 5% indicates that no significant changes have come about in the structure of the fixed carbon between 500°C and 640°C. Such structural changes only occur at much higher temperatures [1,19].

Charring the coals in the presence of NaOH greatly enhances the steam gasification reactivity, due to the incorporation of sodium into the char during pyrolysis, and subsequent catalysis of gasification by sodium [5,8]. The sodium enhances the gasification rates of both the volatile matter (< 5% conversion) and fixed carbon (> 5% conversion). The effect of sodium decreases with time as it volatilizes from the char during gasification. All gasification rates decline with time as the amount of carbon in the fixed bed reactor declines, thereby decreasing the contact time. Charring with NaOH

at 640°C instead of 500°C significantly decreases the gasification reactivity, suggesting that much of the sodium may have vaporized during charring.

The reactivity of the K-Ca oxide catalyst has been proven for graphite, chars, and coals [8,20]. Low catalyst dispersion was observed after nitrate decomposition on graphite, with electron microscopy revealing catalyst particles with diameters mostly around 15 nm [5]. Upon heating in a wet atmosphere, the particles melted and spread along the graphite edges to form a film (film width < 2.5 nm), and the gasification reaction was observed to proceed by erosion of the edges [5]. The chars and cokes consist primarily of randomly polymerized aromatic clusters, so the solid surfaces should behave as graphite edges. The Na-free Illinois #6 chars are relatively hydrophobic, so catalyst dispersal should be similar to that observed for graphite. The Na-containing Illinois #6 chars are more hydrophilic, and the impregnating solution should completely wet the char surface and obtain better dispersal of the catalyst, yielding the large increase in reactivity observed in Fig. 3.

When the carbon solid is obtained by pyrolysis in the absence of NaOH, the K-Ca catalyzed gasification reactivity shows a dependence on the source of carbon in the order subbituminous coal char > bituminous coal char >> petroleum coke (Statfjord or Torrance). The difference in reactivities is associated with differences in the fixed carbon structure and hydrophilicity. The fixed carbon structures in the chars are related to those in the parent coals. The subbituminous coal is made up of smaller aromatic clusters than that of the bituminous coal [18], and the rearrangement of these clusters occur only when pyrolysis takes place above 700°C [1,19]. The 500°C subbituminous char must then be more reactive intrinsically than the 500°C bituminous char, as it is made up of smaller aromatic fragments. The hydrophilicity determines the quality of catalyst dispersion as described above, and is related to the oxygen content in the char as phenoxy and carboxylic groups. The quantity of these groups is related to the desorption of CO (phenoxy) and CO₂ (carboxylic) during thermal treatment [10,18]. Much more CO and CO₂ were observed to desorb from the subbituminous char than from the bituminous char, even after heating to 500°C [18], and the quality of catalyst dispersion on these chars follows accordingly. The petroleum cokes have a very low oxygen content [17] and are highly hydrophobic. The resultant catalyst dispersion on these cokes is expected to be poor, yielding the low catalyzed gasification rates observed. The low reactivity of the cokes makes it impossible to determine differences in their fixed carbon structures.

Pyrolysis in the presence of NaOH increases the hydrophilicity of the carbon solid, facilitating catalyst dispersion. The enhancement is modest in the case of the subbituminous char, as its hydrophilicity is quite high in the absence of NaOH, and is not greatly improved by NaOH treatment. For the other solids, the enhancement due to NaOH is inversely related to the hydro-philicity in the absence of NaOH, being most dramatic for the hydrophobic cokes. Differences in coke reactivity due to carbon structure can now be observed, the Torrance coke being more aromatic and, hence, less reactive [17].

Gasification of the Maya coke (Fig. 6) illustrates that NaHS can be substituted for NaOH and still give the same enhancement of gasification. Sulfur in the effluent can be recovered as H_2S [14,15] making this kind of treatment even more attractive, as it can be used to mediate accumulation and disposal of refinery-derived caustic waste streams containing sulfur.

The pressure independence of the plain char gasification has been observed with another bituminous char, as any enhancements obtained with the higher steam pressure were negated by hydrogen inhibition [13]. The pressure independence of gasification of the K-Ca oxide catalyzed char also is not surprising, as the K-Ca oxide catalyzed reaction on graphite was found to be modestly promoted by steam (rate $\propto (p_{\text{H}_2\text{O}})^{0.5}$) and inhibited by hydrogen (rate $\propto (p_{\text{H}_2})^{-0.2}$) [5]. The pressure enhancement observed in the uncatalyzed gasification of the sodium -containing char is due to a decrease in the rate of sodium volatilization at the higher steam pressure, as the volume fraction of sodium in the effluent stream would be lower. Consequently, the catalytic action of NaOH is preserved for a longer period of time.

Conclusions

It has been demonstrated that the steam gasification rates of coal chars obtained by coal pyrolysis at 500°C are initially high due to gasification of residual volatile matter, and decrease to a rate that reflects the reactivity of the fixed carbon. Pyrolysis at 640°C removes the residual volatile matter from the char and the initial high reactivity associated with it. However, it does not affect the gasification rate at conversions above 5%, as 640°C is not high enough to effect structural changes in the fixed carbon. When the coal is pyrolyzed at 500°C in the presence of NaOH, the resultant chars show

increased gasification rates related to catalysis by Na. This enhancement disappears when all the sodium vaporizes during gasification. Some of the sodium vaporizes from the char when pyrolysis occurs at 640°C. Gasification is accelerated by addition of a K-Ca oxide catalyst to the carbon solid, and the NaOH-derived solids allow better catalyst dispersal during impregnation, further enhancing the catalyzed gasification rate. The effects of NaOH and K-Ca oxide catalyst are realized with many carbon sources, and differences in reactivity are related to the fixed carbon structure and hydrophilicity. Pyrolysis with NaHS yields similar results as for NaOH. In nearly all cases, the gasification rate is indifferent to pressure, as hydrogen inhibition negates any steam promotion at higher pressures. The exception is when increased pressure slows the volatilization of NaOH when it is the only catalyst present.

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Figure Captions

Figure 1. Reactor Set-up: 1) Reactor, 2) Back Pressure Regulator, 3) Mass Flow Controller, 4) Furnace, 5) Reservoir, 6) Pump, 7) Heating Tape, 8) Condenser, 9 - Gas Chromatograph.

Figure 2. Comparison of steam gasification reactivity for chars obtained from Illinois #6 coal at different charring temperatures and with different NaOH loadings. 2a) C conversion vs. time, and 2b) H₂ production rate vs. C conversion. Charring temperature, 500°C (circles), 640°C (squares). NaOH loading, none (closed), 8.5 wt% loading of 10% NaOH solution (crossed) and 20% NaOH solution (open). Gasification temperature, 640°C.

- Figure 3. Comparison of catalyzed and uncatalyzed steam gasification reactivity of Illinois #6 coal chars with different NaOH loadings. 3a) C conversion vs. time, and 3b) H₂ production rate vs. C conversion. Charring temperature, 500°C. NaOH loading, none (circles), 8.5 wt% of 20% NaOH solution (squares). K-Ca catalyst loading, none (closed), 1% (open). Gasification temperature, 640°C.
- Figure 4. Comparison of steam gasification reactivity of different carbon sources (cokes and chars). 4a) C conversion vs. time, and 4b) H₂ production rate vs. C conversion. Statfjord coke (closed circles), Torrance coke (closed squares), Illinois #6 high volatile bituminous coal char (open circles), and Wyoming subbituminous coal char (open squares). Pyrolysis temperature, 450-500°C (cokes) and 500°C (chars). 1% K-Ca catalyst. Gasification temperature, 640°C.
- Figure 5. Comparison of steam gasification reactivity of different carbon sources (cokes and chars) obtained by pyrolysis in the presence of NaOH. 5a) C conversion vs. time, and 5b) H₂ production rate vs. C conversion. Statfjord coke (closed circles), Torrance coke (closed squares), Illinois #6 high volatile bituminous coal char (open circles), and Wyoming subbituminous coal char (open squares). NaOH added prior to pyrolysis, 8.5 wt% of 17% NaOH solution (cokes) or 20 wt% NaOH solution (chars). Pyrolysis temperature, 450-500°C (cokes) and 500°C (chars). 1% K-Ca catalyst. Gasification temperature, 640°C.
- Figure 6. Conversion of C during steam gasification at 640°C of Maya coke obtained with refinery-derived caustic waste (closed squares), with 1% loading of K-Ca catalyst (open squares), and with both caustic and catalyst (asterisks).
- Figure 7. Comparison of steam gasification reactivity at different gasification pressures of Illinois #6 coal chars obtained with 8.5 wt% of 20% NaOH solution added prior to charring. 7a) C conversion vs. time, and 7b) H₂ production rate vs. C conversion. Charring temperature, 500°C. Gasification pressure, 1 atm (0 psig, closed), 7.8 atm (100 psig, open). K-Ca catalyst loading, none (circles), 1% (squares). Gasification temperature, 640°C.

Figure 1

Figure 2a

Figure 2b

Figure 3a

Figure 3b

Figure 4a

Figure 4b

Figure 5a

Figure 5b

Figure 6

Figure 7a

Figure 7b

**Oxidative Coupling of Methane over Mg-Li Oxide Catalysts at
Relatively Low Temperature
—The Effect of Steam**

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Running Title: oxidative coupling of methane over Mg-Li oxide at 600°C

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Abstract

The paper reports on the catalytic oxidative coupling of methane to C₂ and higher hydrocarbons over magnesium-lithium oxide catalyst at low temperatures ($\leq 600^{\circ}\text{C}$), in the presence of steam, and at low space velocity. It is shown that under these conditions active Mg-Li-O catalysts are able to facilitate the oxidative coupling of methane to give 18-22% conversion with selectivity to hydrocarbons $\sim 30\%$. The presence of steam is essential to the formation of the coupling products. In the absence of steam, partial oxidation to form syn-gas becomes dominant at these low temperatures.

**Oxidative Coupling of Methane over Mg-Li Oxide Catalysts
at Relatively Low Temperatures
— The Effect of Steam**

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INTRODUCTION

Previous work (1,2,3) from this laboratory has shown that oxydehydrogenation of methane to hydrocarbons over a calcium-nickel-potassium oxide catalyst occurs at temperatures $\leq 600^{\circ}\text{C}$. It was demonstrated that steam is essential for the coupling and for formation of higher hydrocarbons. Since its discovery by Lunsford et al (4,5), Li/MgO has been intensively studied for its activity in facilitating the oxidative coupling of methane at temperatures $\geq 700^{\circ}\text{C}$. Kimble and Kolts (6) studied the effect of diluents including inert gases such as N_2 , and He, and also CO_2 and water in the oxidative coupling of methane over Li/MgO catalyst at 700°C . They found that inert gases appeared to have no effect on both conversion and selectivity to hydrocarbons. Addition of CO_2 seemed to lead to some formation of carbon monoxide. The presence of steam had a marked effect on the reaction, resulting in an increase in the conversion of methane (from 19% to 22%) and in somewhat improved selectivity to hydrocarbons (from 22% to 23%). In the present work we report the catalytic oxidative coupling of methane to C_2 and higher hydrocarbons over Mg-Li oxide catalysts in the presence of steam at low temperature ($\leq 600^{\circ}\text{C}$) and low space velocity. It appears that the introduction of steam into the reaction mixture of methane and oxygen can result in a significant decrease of reaction temperature required for the oxidative coupling of methane when coupled with long contact time. Our results show that under conditions similar to those used previously (1,2,3), Mg-Li-O catalyst is able to facilitate the oxydehydrogenation to give ~20% conversion with a selectivity to hydrocarbons of close to 30%. The effect of steam at low

temperature 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 appears with certain oxide catalysts the presence of steam can dramatically lower the temperature at which methane coupling can occur.

EXPERIMENTAL

The apparatus used has been described before (2). Methane and oxygen were obtained from Matheson (their purities were better than 99.99%). Distilled water was fed from a syringe driven by a Harvard syringe pump via a heated (at 130°C) transfer line into the reactant stream.

Experiments were carried out using ~ 1.0 g of catalyst. 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 (Hewlett-Packard 5890, packed columns: Carbon Sieve IIS column for TCD, and Porapak-Q column for FID).

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 $250\text{--}550^{\circ}\text{C}$ 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 methods were used. Catalysts (C) and (D) were prepared by incipient wetness impregnation of MgO by 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: 4.1 wt.% 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 ($\geq 700^\circ\text{C}$).

XPS measurements were carried out in a Perkin-Elmer Phi 5300 ESCA system. The samples were prepared by pressing powdered catalysts between a folded pre-cleaned gold foil and then unfolding it. A layer of catalyst sample stuck on the foil and was analyzed. The conditions employed to collect XPS data were: Al anode (400 W); pass energy 35.7 eV; acquisition time ≥ 20 min; angle 45° .

RESULTS AND DISCUSSION

MATERIAL BALANCE

In order to obtain proper materials balances, an inert tracer, nitrogen was used as described previously (3). The results of a typical run in the presence of steam using the internal standard are presented in Table I.

The deficits in the carbon and oxygen balances ($\sim 16\%$ and $\sim 90\%$, respectively in the first four hours must be due to products retained on the catalyst which are not detected in the outlet stream. The consumption of methane and oxygen for the formation of carbonate is in a ratio that is consistent with the deficits in the gas phase carbon and oxygen balances. In addition, the formation of a carbonaceous residue might occur. Its formation requires oxygen to remove hydrogen to form water which could not be quantified because of the use of excess steam. This would cause poor

oxygen balances. The lack of data on the amount of carbonaceous materials formed could lead to poor carbon balance.

EFFECTS OF CATALYST COMPOSITION AND PREPARATION

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 2

MgO alone produced mainly carbon dioxide. Introduction of potassium into MgO did not improve its selectivity to hydrocarbons, and caused a significant decline in catalyst activity. 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 higher selectivity to hydrocarbons ($\geq 30\%$) and higher activity (18% vs. 15%). Li/MgO catalysts prepared by incipient wetness impregnation of MgO with LiNO₃ aqueous (C, D) solution showed either no change or a slight increase in selectivity to hydrocarbons compared to the parent MgO catalyst and a minor decrease in catalyst activity. Catalyst (E) obtained from Lunsford group prepared by impregnation of MgO with Li₂CO₃ aqueous solution gave a selectivity to hydrocarbons about equal to catalysts (A) and (B) prepared by co-decomposition but was much less active. This clearly indicates that the procedure used for catalyst preparation plays a crucial role.

The high activity of MgO catalyst may be a reflection its high surface area. Its surface area is more than one order of magnitude greater than the Li/MgO and K/MgO. The typical surface area of Li/MgO was around $1 \text{ m}^2 \cdot \text{g}^{-1}$ while that of MgO was $15 \text{ m}^2 \cdot \text{g}^{-1}$. 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 higher activity and better selectivity to hydrocarbons, whereas incipient wetness impregnation of magnesium oxide

with lithium nitrate solution 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 relatively 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 (7) 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.

PRODUCT DISTRIBUTION

Table 3 gives results of the hydrocarbon distribution from a typical run at 600°C during ca. 3-4 hours. Among the hydrocarbon products, ethylene and ethane are dominant. 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.

EFFECT OF STEAM

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 enhances the selectivity to hydrocarbons. In addition to this, the presence of steam also improved the catalyst's activity, particularly at lower reaction temperatures. Another effect of steam is to increase the olefin to paraffin ratio. However, at higher reaction temperatures, the effect of steam is less significant in terms of both activity and selectivity. The effect of steam is

greater for catalysts prepared by nitrate co-decomposition (e.g. catalyst Li/MgO (A)) than for those prepared by incipient wetness (e.g. catalyst (D))

TURNOVER FREQUENCY AND NUMBER OF TURNOVERS

In order to determine whether a reaction is catalytic or stoichiometric and how fast a reaction is, it is necessary to estimate the number of turnovers (number of molecules transformed per active site during the active period of the site) and the turnover frequency (number of molecules converted per active site per second).

Because the complexity of multi-component oxides and the poor understanding of their surface, it is impossible to define and measure the number of active sites on the surface of catalysts of this kind. For this reason, we assumed that all the surface oxygen sites are active sites. This, of course, dramatically overestimates the total number of active surface sites. Consequently, the real turnover frequency and number of turnovers should be much greater than the experimental values obtained.

Based on an assumed of 10^{19} † oxygen sites per square meter, the turnover frequency and number of turnovers for a typical run at 600°C before the catalyst died are 2×10^{-2} molecules $\cdot$ sec $^{-1}$ $\cdot$ site $^{-1}$, and 4×10^2 molecules $\cdot$ site, respectively. The turnover frequency obtained here is not great compared to that of majority of industrially important catalytic processes, being of the order of one molecule per second, but it is not an insignificant value. A number of turnovers greater than 10^3 is usually regarded as significant. In view of the unlikely assumption that all surface sites are catalytically active, a number of turnovers of 4×10^2 will probably correspond to more than 10^3 turnovers of an actual active site. It is therefore concluded that the reactions observed are catalytic.

† This value is obtained based on an assumption that each oxygen atom occupies $12.5 \text{ \AA}^2$ which is derived from a bond length of Mg-O of $2 \text{ \AA}$ and the crystal structure of MgO.

MECHANISTIC CONSIDERATION IN METHANE COUPLING

The relatively high selectivity to hydrocarbons (~30%) at lower temperature ($\leq 600^\circ\text{C}$) compared to the widely used high temperature ($\geq 700^\circ\text{C}$) also suggests 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 (8) and others (9,10). 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 believe 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 $550\text{--}600^\circ\text{C}$, which thermally decomposes into O^- at temperatures above $550\text{--}600^\circ\text{C}$ (8). 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 the 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 compared to that at 600°C (cf. Table 4). Coupling activity observed at temperatures $550\text{--}600^\circ\text{C}$ 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 $550\text{--}600^\circ\text{C}$ (8-12). 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 to ($\text{O}_2^{2-} \longrightarrow \text{O}^- + \text{O}^-$) whereby one O^- remains bound to the vacancy while the other O^- becomes unbound as suggested by Freund et al (11, 13). Therefore, the presence of steam is necessary to produce O^- at temperature around $550\text{--}600^\circ\text{C}$ 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 (14). However, at high temperatures, 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 temperatures may not favor the formation of surface OH⁻ groups.

XPS measurements were used to reveal the changes of the surface of catalyst before and after use, and the differences between the surfaces of an active and a non-active catalyst. Figure 1 presents the Li 1s XPS spectra of a Li-Mg oxide catalyst before and after use. The spectra show that there was a significant decline of the Li 1s signal after the catalyst had been used at 600°C for the oxidative coupling of methane in the presence of steam. This decline of Li signal suggests the disappearance of surface lithium species. This could mean loss of lithium either by evaporation as suggested by some investigators (15) or relocation of surface lithium into the bulk. The fact that the used catalysts can be regenerated by treatment at temperatures higher than the reaction temperature appears to indicate that lithium was not permanently lost since it is difficult to conceive how surface lithium can be restored by such a treatment. The change of concentration of surface lithium revealed by XPS may indicate that the deactivation of the catalyst could be caused by temporary loss of surface Li species.

The O 1s XPS spectra of an active, a non-active and a used catalysts are given in Figure 2. The spectrum of the non-active Li-Mg oxide catalyst consists of two single peaks at binding energies of 532.5 and 534.0 eV, indicating there were probably two types of oxygen species present on the catalyst surface, the relative proportions of which were 53% and 47%, respectively. From the spectrum of the active Li-Mg oxide catalyst, two peaks may be resolved, at binding energies of 532.4 and 534.1 eV. Within experimental errors, the two oxygen peaks at 532.5 and 534.0 eV of the non-active catalyst and the two at 532.4 and 534.1 eV of the active catalyst may be regarded as the same, due to the same two types of oxygen species, referred to as O_l and O_d, respectively. Thus, the only difference between an active and a non-active catalysts is the relative concentration of the two types of oxygen species. It is generally believed that the oxygen species having low binding energy (here 532.4 eV) is due to the lattice oxygen, while the one having

higher binding energy (534.1 eV) may be the oxygen species responsible for the high activity of oxidative coupling of methane (16). The latter was also identified in the used catalyst. The spectra of the fresh and used catalysts reveal that the relative concentration of the two oxygen species changed dramatically. After use, they changed from O_d : 75%, O_l : 25%, to O_d : 52%, O_l : 48%. It should be mentioned that there is virtually no change of surface area ($0.76 \text{ m}^2 \cdot \text{g}^{-1}$ of fresh catalyst versus $0.73 \text{ m}^2 \cdot \text{g}^{-1}$ of spent catalyst). This change may explain the change of product distribution from relatively high selectivity to hydrocarbons to selectivity to CO_x . To achieve high selectivity to coupling product a high concentration of O_d species is required. The difference between the active and non-active catalyst was the concentration of surface oxygen species O_d . The active catalyst which gave high selectivity to hydrocarbons had much greater concentration of O_d . In terms of composition of surface oxygen species, there was basically no difference between the non-active catalyst and the used (deactivated) catalyst, suggesting that a high concentration of O_d is necessary to a catalyst of high selectivity to coupling products. It should be mentioned that a less selective catalyst has about the same surface area as one which was active and selective. This oxygen species O_d may be related to the O^- which has been proposed for a rare earth element doped MgO catalyst based on XPS data (16).

CONCLUSIONS

The oxydehydrogenation of methane to hydrocarbons with relatively high selectivity can occur over Li/MgO catalyst in the presence of steam at low temperature ($\leq 600^\circ\text{C}$). The presence of steam appears to be essential for the formation of the coupling products. Its presence also results in somewhat higher conversion of methane and better olefin selectivity. Li/MgO catalysts exhibit similar behavior as Ca-Ni-K oxide catalysts. A high level of surface oxygen species having a binding energy of 534.1 eV was identified by XPS technique in the Li-Mg oxide catalyst giving high selectivity to coupling products.

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FIGURE CAPTIONS

Fig. 1 Li_{1s} and Mg_{2p} XPS spectra of a fresh (i); and a used (ii) Li-Mg oxide catalyst.

Fig. 2 O_{1s} XPS spectra of a non-active Li-Mg oxide catalyst (i); and an active Li-Mg oxide catalyst: fresh (ii); used (iii).

Table 1 Product distribution obtained using internal standard (reaction of CH₄ with O₂ in the presence of steam over Li/MgO (A) catalysts at 600°C)

Time on Steam (h)	<u>Conversion</u> CH ₄ (mol.%)	<u>Selectivity</u>			<u>Balance</u>	
		HC ^a (mol.%)	CO ₂ (mol.%)	Undetected (mol.%)	Carbon (%)	Oxygen (%)
1.2	22	30	3	68	85	12
2.5	24	31	3	69	83	11
3.5	23	29	4	70	84	12
6.5	18	10	73	16	97	86

a, HC: hydrocarbon products;

Table 2 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	Hydrocarbons	CO _x ^b
Li/MgO (A)	Mg ₂ Li ₁ O _x	calcination ^c	18	30	70 (0)
Li/MgO (B)	Mg ₂ Li ₁ O _x	calcination	17	31	69 (0)
Li/MgO (C)	Mg ₂ Li ₁ O _x	incipient wetness ^d	14	16	84 (0)
Li/MgO (D)	Mg ₂ Li ₁ O _x	incipient wetness ^e	13	12	88 (0)
Li/MgO (E)	Mg ₄ Li ₁ O _x	impreg- nation/ ^f	11	28	72 (1)
K/MgO (F)	Mg ₂ K ₁ O _x	calcination ^c	9	8	92 (3)
MgO (G)	MgO	calcination ^c	15	12	88 (1)

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

b, amount of carbon monoxide in brackets; CO_x selectivity is the sum of CO and CO₂ in gas phase and CO₂ on catalyst due to the formation of carbonate;

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;

Table 3 Hydrocarbon Distribution of the Gas Phase Product for the Reaction of Methane with Oxygen in the Presence of Steam over Li/MgO(A) Catalyst at 600°C ^a

Time on Steam/ min.	<u>Selectivity to Hydrocarbons and Carbon Oxides %</u>				
	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄₊
65	35	53	4	6	2
145	36	53	4	5	2
225	29	65	2 [*]	3	1

a, CH₄: 1.5 cm³•min⁻¹; O₂: 0.5 cm³•min⁻¹; H₂O: 3.3 cm³•min⁻¹;

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

Temperature /°C	Steam	<u>Conversion%</u>	<u>Selectivity %</u>		
		CH ₄	CO _x ^b	Hydrocarbons	C ₂ '/C ₂ ^o
550	yes	6	85 (0)	15	< 0.2
600	yes	18	70 (0)	30	0.6
600	no	14	95 (2)	5	0.3
650	yes	19	77 (3)	23	0.8
650	no	16	81 (2)	19	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; CO_x selectivity is the sum of CO and CO₂ in gas phase and CO₂ on catalyst due to the formation of carbonate;

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

Temperature /°C	Steam	<u>Conversion%</u>	<u>Selectivity %</u>	
		CH ₄	CO _x ^b	Hydrocarbons
600	no	11	94	6
600	yes	13	88	22
650	no	15	90	10
650	yes	17	80	20

a, Methane: 1.5 cm³•min⁻¹; O₂: 0.5 cm³•min⁻¹; H₂O: 3.3 cm³•min⁻¹;

b, CO_x selectivity is the sum of CO and CO₂ in gas phase and CO₂ on catalyst due to the formation of carbonate;

**DATE
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8 / 26 / 93

END