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

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The paper reports on the catalytic oxidative coupling of methane to C_2 and higher hydrocarbons over magnesium–lithium oxide catalyst at low temperatures (≤600°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 ~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. © 1993 Academic Press, Inc.

INTRODUCTION

Previous work (*1–3*) from this laboratory has shown that oxydehydrogenation of methane to hydrocarbons over a calcium–nickel–potassium oxide catalyst occurs at temperatures ≤600°C. It was demonstrated that steam is essential for the coupling and for formation of higher hydrocarbons. Since its discovery by Lunsford and coworkers (*4*, *5*), Li/MgO has been intensively studied for its activity in facilitating the oxidative coupling of methane at temperatures ≥700°C. Kimble and Kolts (*6*) showed that the maximum differences due to the presence of steam at 700°C are: selectivity to ethane decreased by about 10%, selectivity to ethylene increased by about 20%, and conversion of methane increased by about 20%. Total selectivity to hydrocarbons increased by about 5%. 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 (≤600°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. While the effect of steam on the conversion of methane at high temperature (≥650°C) is only marginal, it resulted in a significant increase of selectivity and conversion at 600°C. A higher olefin-to-alkane ratio is also obtained. Our results show that under conditions similar to those used previously (*1–3*), 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 (≥700°C) and short contact times. It appears that 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.

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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 ($2.5\ cm^3 \cdot min^{-1}$) for a period of 16–20 h then cooled to the required reaction temperature before steam and methane were introduced. A feed composition of $CH_4:O_2:H_2O = 3:1:6.5$ mol and a total flow rate of $5.4\ cm^3 \cdot min^{-1}$ 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 preground and well homogenized mixture of $Mg(NO_3)_2 \cdot 6H_2O$ (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 250–550°C, while calcination was conducted at 680°C for 14 h. 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 $Mg_2Li_1O_x$ was used. For comparison, a standard Li/MgO (Li: 4.1 wt% or equivalent to $Mg_4Li_1O_x$) 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 (≥700°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 precleaned 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 material 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 1.

TABLE 1

Product Distribution Obtained Using Internal Standard (Reaction of CH_4 with O_2 in the Presence of Steam over Li/MgO (A) Catalysts at 600°C)

Time on stream (h)	Conversion CH_4 (mol %)	Selectivity			Balance	
		HC[a] (mol %)	CO_2 (mol %)	Undetected (mol %)	Carbon (%)	Oxygen (%)
1.2	22	30	3	67	85	12
2.5	24	31	3	66	83	11
3.5	23	29	4	67	84	12
6.5	18	10	73	17	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 (%) CH_4	Selectivity (%)	
				Hydrocarbons	CO_x[b]
Li/MgO (A)	$Mg_2Li_1O_x$	Calcination[c]	18	30	70 (0)
Li/MgO (B)	$Mg_2Li_1O_x$	Calcination	17	31	69 (0)
Li/MgO (C)	$Mg_2Li_1O_x$	Incipient wetness[d]	14	16	84 (0)
Li/MgO (D)	$Mg_2Li_1O_x$	Incipient wetness[e]	13	12	88 (0)
Li/MgO (E)	$Mg_4Li_1O_x$	Impregnation[f]	11	28	72 (1)
K/MgO (F)	$Mg_2K_1O_x$	Calcination[c]	9	8	92 (3)
MgO (G)	MgO	Calcination[c]	15	12	88 (1)

[a] Data taken from results obtained after 90 min of time on stream.

[b] Amount of carbon monoxide in brackets; CO_x selectivity is the sum of CO and CO_2 in gas phase and CO_2 on catalyst due to the formation of carbonate.

[c] Prepared from nitrates by calcination at 680°C.

[d] Incipient wetness of MgO prepared from $Mg(NO_3)_2 \cdot 6H_2O$ by $LiNO_3$ aqueous solution, then calcined at 680°C.

[e] Incipient wetness of MgO (ultrafine single crystal from Ube Industries Ltd.) by $LiNO_3$ aqueous solution, then calcined at 680°C.

[f] Prepared from Li_2CO_3 and MgO: dried at 140°C for 14 h, then $5°C \cdot min^{-1}$ to 500°C for 2 h and finally, $5°C \cdot min^{-1}$ to 700°C for 12 h.

The deficits in the carbon and oxygen balances (~16 and ~90%, respectively) in the first 4 h 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 codecomposition 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 (≥30%) and higher activity (18% vs 15%). Li/MgO catalysts prepared by incipient wetness impregnation of MgO with $LiNO_3$ 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 the Lunsford group prepared by impregnation of MgO with Li_2CO_3 aqueous solution gave a selectivity to hydrocarbons about equal to catalysts (A) and (B) prepared by codecomposition 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 of 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 $m^2 \cdot g^{-1}$, while that of MgO was 15 $m^2 \cdot g^{-1}$. The treatment of MgO with $LiNO_3$ 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 noted 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 Ohano and 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 change, 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 h. 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.

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 stream (min)	Selectivity to hydrocarbons (%)				
	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4-
65	35	53	4	6	2
145	36	53	4	5	2
225	29	65	2	3	1

[a] CH_4, 1.5 $cm^3 \cdot min^{-1}$; O_2, 0.5 $cm^3 \cdot min^{-1}$; H_2O, 3.3 $cm^3 \cdot min^{-1}$.

Effect of Steam

Tables 4 and 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 codecomposition (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

TABLE 4

Effect of Steam on Reaction of Methane with Oxygen over Li/MgO (A) Catalyst[a]

Temperature (°C)	Steam	Conversion (%) CH_4	Selectivity (%)		
			CO_x[b]	Hydrocarbons	$C_2^=/C_2^\circ$
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 $cm^3 \cdot min^{-1}$; O_2, 0.5 $cm^3 \cdot min^{-1}$; H_2O, 3.3 $cm^3 \cdot min^{-1}$.

[b] Amount of carbon monoxide in brackets; CO_x selectivity is the sum of CO and CO_2 in gas phase and CO_2 on catalyst due to the formation of carbonate.

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 10^{19} oxygen sites per square meter[1], the turnover frequency and number of turnovers for a typical run at 600°C before the catalyst died are 2×10^{-2} molecules $\cdot$ s^{-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.

Mechanistic Consideration in Methane Coupling

The relatively high selectivity to hydrocarbons (~30%) at lower temperature (≤600°C) compared to the widely used high temperature (≥700°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^- spe-

TABLE 5

Effect of Steam on Reaction of Methane with Oxygen over Li/MgO (D) Catalyst[a]

Temperature (°C)	Steam	Conversion (%) CH_4	Selectivity (%)	
			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 $cm^3 \cdot min^{-1}$; O_2, 0.5 $cm^3 \cdot min^{-1}$; H_2O, 3.3 $cm^3 \cdot min^{-1}$.

[b] CO_x selectivity is the sum of CO and CO_2 in gas phase and CO_2 on catalyst due to the formation of carbonate.

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[1] This value is obtained based on an assumption that each oxygen atom occupies 12.5 Å^2, which is derived from a bond length of Mg–O of 2 Å and the crystal structure of MgO.

cies 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, Na_2O/CaO, La_2O_3/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 temperatures below 550–600°C, which thermally decomposes into O^- at temperatures above 550–600°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 550–600°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 (*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 them undergo homolytic splitting to form O_2^{2-}; these dissociate at above 550°C according ($O_2^{2-} \rightarrow O^- + O^-$) whereby one O^- remains bound to the vacancy while the other O^- becomes unbound as suggested by Freund and coworkers (*11, 13*). Therefore, the presence of steam is necessary to produce O^- at 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 (*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.

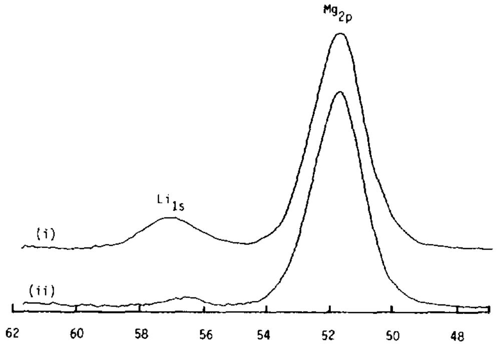

FIG. 1. Li_{1s} and Mg_{2p} XPS spectra of a fresh (i) and a used (ii) Li–Mg oxide catalyst.

XPS measurements were used to reveal the changes of the catalyst surface before and after use, and the differences between the surfaces of an active and a nonactive 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 O1*s* XPS spectra of an active, a nonactive and a used catalyst are given in Fig. 2. The spectrum of the nonactive Li–Mg

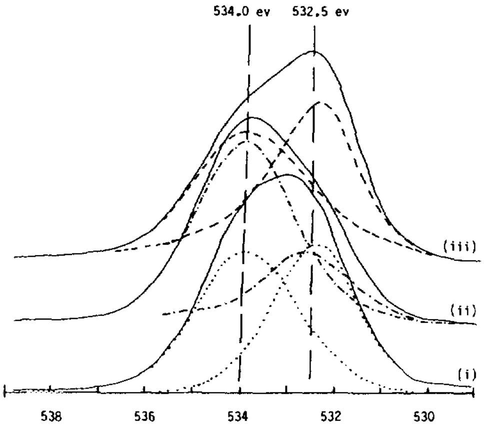

FIG. 2. O_{1s} XPS spectra of a nonactive Li–Mg oxide catalyst (i) and an active Li–Mg oxide catalyst: fresh (ii) and used (iii).

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 nonactive 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 nonactive catalyst 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 $m^2 \cdot g^{-1}$ of fresh catalyst versus 0.73 $m^2 \cdot g^{-1}$ 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 nonactive 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 nonactive 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 (≤600°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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