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Effects of Superbasic Catalysts Prepared by Promoting MgO with Bialkali Metal Compounds on the Oxidative Coupling of Methane

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The improvement in methane conversion, C_2 selectivity, and stability with time-on-stream for the oxidative coupling of methane (OCM) has been studied by employing superbasic catalysts prepared by promoting MgO with various binary alkali metal compounds. The performance of the resulting catalysts is found to strongly depend on the nature of the alkali metal compounds forming the pair, the promoter contents, and the appropriate reaction conditions (temperature, pseudo-contact time, etc.). In addition, the choice of a proper MgO offers a considerable effect in improving the overall performance of the resulting catalysts. The most effective catalytic systems are MgO (prepared via the sol–gel process) promoted with the bialkali metal compounds of LiA + NaA (A = Cl^-, OH^-, Ac^-, CO_3^{2-}, or NO_3^-), LiA + CsA, or NaA + CsA containing total loadings of alkali metal compounds of 10 or 20 mol% with equal molar loading from both compounds. Any bialkali-promoted system containing potassium or rubidium was less effective than the aforementioned systems. An appreciable C_2 yield as high as 19.8% was obtained at a methane conversion of 23.8 mol% over (10 mol% NaCl + 10 mol% CsCl)/MgO under atmospheric pressure, at 750°C, P_{CH_4} = 608 Torr, CH_4/O_2 molar ratio = 4 (without any diluent) and a space velocity of 15,000 $cm^3\ g^{-1}\ h^{-1}$. Moreover, the methane conversion and the total C_2 selectivity, after a slight initial decrease, remain almost unchanged for a period of 60 h. In contrast, the maximum C_2 yield over any monoalkali-promoted system never exceeded 5.5% under the same conditions and their stability with time-on-stream was not as prominent. The relatively high performances of the bialkali-metal-compound-promoted MgO compared to those of the respective monoalkali-promoted systems are likely to be related to the synergistic increase in the surface basicity (superbasicity) caused by the enrichment of the surface with the alkali. The presence of a second alkali noticeably enhances the enrichment. The relationship between the catalytic performances and the physicochemical characteristics of the catalysts revealed by XRD, XPS, and basicity measurements (both by the thermal desorption of CO_2 and the benzoic acid titration methods) is explored.

INTRODUCTION

The direct one-step conversion of methane to C_2 hydrocarbons by catalytic oxidative coupling is a potential route for the production of useful chemicals and fuels. The reaction is favorable in the temperature range of 650–850°C in the presence of solid catalysts with ethane, ethylene, carbon dioxide, carbon monoxide, and water as the major products. A growing number of solid materials (*1*, *2*) have been found to be effective in enhancing the C_2 hydrocarbon selectivity, but suppression of the undesirable carbon oxides is still a challenge. It has been suggested (*3*) that basic catalysts are suitable for high C_2 selectivities by reducing the undesirable CO_x (x = 1, 2) formation. In general, the alkali-promoted metal oxides, alkaline earth oxides, rare earth oxides, and mixed metal oxides, which have been found to be effective for the oxidative coupling of methane (OCM), possess basic properties. This brings evidence that the basic sites are beneficial for the selective formation of C_2 hydrocarbons.

The requirement of high surface basicity for achieving an appreciable C_2 selectivity

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has been investigated by a number of researchers (*3–22*). Baerns and Co-workers (*3*, *5–7*) reported that a direct relationship exists between the C_2 selectivity and the basicity of the alkaline earth oxides. The C_2 selectivity increases in the series BeO, MgO, CaO, SrO, and BaO in accordance with the increase in the bulk basicity of these materials. The C_2 selectivities were found to be higher for the alkaline earth oxides than for the respective salts. This indicates that the nature of the anion also plays a role in determining the basicity and ultimately selectivity.

Matsuda *et al.* (*8*) found that the basicity of MgO increases when doped with sodium compounds and this enhancement of the basicity is partly responsible for the high C_2 selectivity. They attributed this basicity increase to the perturbation of the charge distribution on MgO upon doping with the alkali metal ions, according to the acid–base theory (*9*). Sokolovskii and co-workers (*10*, *11*) observed that both the C_2 selectivity and methane conversion over the oxides or phosphates of Mg, Ca, Sr, and Ba increases with increasing basicity, measured by the benzoic acid adsorption method. Choudhary and co-workers (*12*, *13*) measured the basicity and the base strength distribution on alkaline earth or rare earth oxides by stepwise thermal desorption of carbon dioxide and found that a "complex" relationship exists between the catalytic activity/selectivity and the acidity and basicity of the catalysts.

Recently, it has been demonstrated (*14*) that the C_2 selectivity increases with the basicity of the alkaline earth oxides or rare earth oxides, expressed in terms of the decomposition temperature of the carbonate. The basicity of MgO, one of the most widely studied oxides in the OCM process, could be improved by incorporating a certain amount of CaO (this was estimated from the wavenumber difference of the IR absorption bands of the surface carbonates), thereby enhancing the C_2 selectivity (*15*). The relevance of the basicity of OCM catalysis has also been recognized by other researchers (*16–22*).

The existence of base analogs of the solid superacids was suggested almost ten years ago by Kijenskii and Malinowskii (*23*, *24*). The catalytic activity of such superbases in the dehydrogenation of isopropylbenzene was extremely high. According to Ref. (*23*), the term "superbase" is used to denote a base strong enough to detach the proton from a hydrocarbon molecule, such as triphenyl methane (pK_a of acid indicator 33) or methane ($pK_a = 40$). The base strength H_- of a superbase should therefore lie in the range $40 > H_- > 33$. However, according to Tanabe *et al.* (*25*), materials which possess basic sites stronger than 26 can be termed superbases (the latter value is in conformity with the definition of solid superacids). A superbase can be obtained by promoting an oxide such as MgO or Al_2O_3 with bialkali metals (*23*).

The concept of superbasic materials has prompted us to investigate their catalytic influence on the OCM process, since basicity has already been shown to be effective for this reaction. We prepared superbasic oxides by depositing various binary alkali metal compounds on MgO and calcining at high temperatures. In the present paper, it is shown that such superbasic materials are more effective in the OCM process than the corresponding monoalkali-compound-promoted materials. A synergistic effect was found for both the basicity as well as for the activity and C_2 selectivity when binary mixtures of alkali compound are employed, instead of the corresponding monoalkali compounds.

EXPERIMENTAL

Catalyst Preparation

The following reagents were used for the preparation of MgO and of mono- and bialkali-metal-compound-promoted MgO: $Mg(OEt)_2$, $Mg(NO_3)_2$, HCl, C_2H_5OH, $(NH_4)_2CO_3$, MgO, and alkali precursors MOH, M_2CO_3, MNO_3, MCl, or MCH_3COO

(where M = Li, Na, K, Rb or Cs). All reagents were of 99+% purity (Aldrich) and were used as received.

MgO was prepared by a sol–gel method, according to the procedure presented in Ref. (*26*). Briefly, the method involves the hydrolysis of magnesium ethoxide dissolved in ethanol in the presence of an acid (HCl, pH = 3) under constant stirring until a gel is formed, followed by drying at 80°C for 12 h. The resulting MgO is calcined at 750°C for 15 h, followed by pressing, crushing, and sieving to 80-mesh particle sizes.

Onto this MgO powder mono- or bialkali metal ions were deposited by conventional impregnation, using five different alkali precursors (MOH, M_2CO_3, MNO_3, MCl, or MCH_3COO, where M = Li, Na, K, Rb or Cs). For the deposition of monoalkali metal ions, an aqueous solution of the alkali metal salt was introduced into an aqueous slurry of MgO under vigorous stirring at 80°C, followed by evaporation to dryness, drying overnight at 120°C, calcination in air at 750°C for 15 h, powdering, pressing, crushing, and sieving to 80-mesh particle sizes. For the deposition of bialkali metal ions, an aqueous solution of any two alkali metal salts (prepared by dissolving the salts simultaneously in distilled water) was used.

Another batch of the aforementioned catalysts was prepared by gel-precipitation. In this method, the deposition of the monoalkali metal ions was carried out by introducing an aqueous solution of the alkali metal salt into a solution of magnesium nitrate, followed by the dropwise addition of an $(NH_4)_2CO_3$ solution (precipitating agent) with vigorous stirring until a precipitate settled down. This was followed by filtering, washing, drying, calcination, pressing, crushing, and sieving as above. For the deposition of the bialkali metal ions, an aqueous solution of any two alkali metal salts was used as in impregnation. The alkali metal loading usually was 10 mol% for the monoalkali deposition. For the bialkali metal ions the total metal loading was also usually 10 mol%, comprising an equal molar amount of both compounds, except when the effect of the loading was studied.

Unless otherwise stated, the results presented were obtained over alkali-promoted catalysts prepared by the impregnation method, using MgO (sol–gel) as the support, since their performances were much better than those prepared by the gel-precipitation method.

Catalyst Screening

The methane coupling reactions were performed in the temperature range 650–800°C under atmospheric pressure by cofeeding the undiluted reaction gases (P_{CH_4} = 608 Torr and P_{O_2} = 152 Torr) into a high purity alumina tube reactor (6 mm i.d., 30 cm long) mounted horizontally and heated by a single-zone tube furnace (8-cm-long hot zone) with a built-in thermocouple. The details and the schematic diagram of the reactor have been published previously (*27*). Usually, 200 mg of calcined catalyst sandwiched between quartz wool plugs were placed in the center of the reactor tube, which was connected to the gas inlet and outlet systems through cajon fittings. An inconel sheathed K-type thermocouple was located into the catalyst bed, measuring the temperature with an accuracy of ±3°C. High purity methane and oxygen (all 99.9% purity, Linde Division) were used without any diluent and additional purification. The flow of each gas was controlled by a variable constant differential flow controller and the total flow rate measured at the inlet of the reactor was 50 ml/min (NTP). Under the conditions employed, the empty reactor produced less than 1% methane conversion.

Product Analysis

The reaction products, after separated from water by passing through a heptanol–liquid nitrogen bath (−30°C), were sampled on-line using an automatic 10-port sampling valve (Valco) and analyzed by a gas chromatograph (PE Sigma 2000) fitted with thermal conductivity and flame ionization detectors and attached to a PE 3600 data station. A Chromosorb 102 column (6 ft × 1/8 in, 25° isothermal) was used to analyze O_2, CH_4, CO_2, C_2H_4, C_2H_6, and residual H_2O (if any), a molecular sieve 5A column (6 ft × 1/8 in, 25° isothermal) to separate O_2, N_2, CH_4 and CO, and a Porapak T column (6 ft × 1/8 in, programmed 25–140°C) to analyze CH_4, C_2H_4, C_2H_6, and C_{3+} (hydrocarbons $\geq C_3$) hydrocarbons. The latter products were less than 1 mol% when explicitly monitored. Nitrogen or argon was used as an internal standard. The response factors for the reactants and products were determined using certified calibration gases (Linde Division). The carbon mass balance was greater than 95% and the oxygen mass balance 98% in all experiments. The conversion of methane is expressed as the fraction of moles of methane reacted. The selectivity is the ratio of the number of moles of methane converted to a particular product to the total number of moles of methane reacted. The yield is the product of the conversion and the selectivity.

Catalyst Characterization

The calcined and postcatalysis samples were characterized by (i) surface area measurement (BET method), (ii) X-ray diffraction (XRD) analysis, (iii) atomic absorption spectrophotometry (AAS), (iv) X-ray photoelectron spectroscopy (XPS), and (v) basicity/base strength distribution measurements. The surface areas of the calcined samples were determined by the BET method using the adsorption of nitrogen gas at the liquid nitrogen temperature (77 K). The crystalline phase of some samples was determined with a Siemens Analytical X-ray instrument using a CuK_α source of radiation. The alkali metal ion loadings (as oxides) on the MgO support of some calcined and postcatalysis samples were determined by the AAS (flame) method (Perkin–Elmer 3030). The surface compositions and the valence states of the elements present in some samples were studied by XPS using a PHI 500 spectrophotometer. The details of the procedure have been given in Refs. (*27*, *28*).

The basicity and the base strength distribution of the solid catalysts were determined by two methods: benzoic acid titration using indicators, and the gaseous acid (CO_2) adsorption followed by its stepwise thermal desorption (STD). In the benzoic acid titration method (*25*, *29*, *30*), the amount of basic sites were measured by titrating a suspension of a solid in benzene with benzoic acid dissolved in benzene, using an acid indicator which has been adsorbed in its conjugated basic form. The benzoic acid titres represent the amounts of basic sites (in mmol g^{-1}) with a basic strength corresponding to the pK_{BH} value of the indicator used. For the reaction of an acid indicator BH with a solid base $\overline{B}$ (*25*),

$$BH + \overline{B} \leftrightarrows B^- + \overline{B}H^+,$$

the base strength H_- of $\overline{B}$ is given by the equation

$$H_- = pK_{BH} + \log([B^-]/[BH]),$$

where [BH] is the concentration of the acid indicator and $[B^-]$ the concentration of the dissociated indicator. The value of the basic strength on the surface is given by the pK_{BH} value of the adsorbed indicator for which the intermediate color appears, i.e., when $[B^-]/[BH] \cong 1$. The indicators which are used for this method are listed in Ref. (*25*).

In the STD method, the procedure is as described in Refs. (*31*, *32*). Briefly, high purity CO_2 (99.995%) is chemisorbed on the solid catalyst (precalcined in situ at 850°C in a flow of helium for 15 h) at 50°C (1.0 g packed in an alumina reactor) in the flow of He (20 cm^3/min), followed by heating it from 50 to 850°C in a number of successive temperature steps (50–150°C, 150–300°C, 300–500°C, 500–700°C, and 700–850°C) at a heating rate of 10°C/min. When the maximum temperature of the respective step was attained, the heating was held at that temperature for 15 min until no additional

CO_2 desorbed. The analysis of the evolved gas was carried out with a GC-MS (Hewlett–Packard MSD5971) fitted with a Poraplot Q column (25 m). The amount of CO_2 desorbed in each step was determined by a TCD suitably calibrated using helium as a carrier gas. The reproducibility of the method was 95%.

RESULTS

Catalytic Performance

Pure MgO prepared by the sol–gel method [denoted MgO (s-g)] or mono- or bialkali-metal-compound-promoted MgO are low-surface-area (<15 m^2/g) crystalline materials. Some physicochemical characteristics of the calcined MgO and mono- or bialkali-metal-hydroxide-promoted MgO are presented in Table 1. Upon promoting MgO with the alkali metal hydroxides, the surface areas of the resulting materials decrease. These decreases are more noticeable with the bialkali-promoted MgO than the monoalkali-promoted ones.

TABLE 1

Some Physicochemical Characteristics of the MgO Supported Mono- and Bialkali Metal Compounds after Calcination at 750°C, 15 h

Catalyst[a]	Surface area (m^2/g)	Alkali compound loading[b] (mol%)
1. MgO (s–g)	14.5	—
2. LiOH/MgO	7.0	10
3. NaOH/MgO	8.2	10
4. KOH/MgO	7.5	10
5. RbOH/MgO	8.5	10
6. CsOH/MgO	8.0	10
7. LiOH + NaOH/MgO	6.0	5 + 5
8. LiOH + KOH/MgO	5.5	5 + 5
9. LiOH + RbOH/MgO	6.5	5 + 5
10. LiOH + CsOH/MgO	6.8	5 + 5
11. NaOH + KOH/MgO	6.5	5 + 5
12. NaOH + RbOH/MgO	6.2	5 + 5
13. NaOH + CsOH/MgO	7.0	5 + 5
14. KOH + RbOH/MgO	6.4	5 + 5
15. KOH + CsOH/MgO	6.5	5 + 5
16. RbOH + CsOH/MgO	6.5	5 + 5

[a] Crystalline phases identified by XRD are MgO only, except for Sample #3, which showed an additional phase of Na_2CO_3.

[b] AAS analysis showed that the alkali loadings are approximately the same before and after calcination of the catalysts, except for Li and Rb which exhibited drastic losses.

In spite of the decreases in surface area, the catalytic performances of the bialkali promoted MgO were significantly higher than those of the monoalkali-promoted MgO or pure MgO. The methane conversions, product selectivities, and C_2 yields obtained at 750°C over pure MgO (s-g) and MOH, MCl, MAc, M_2CO_3, or MNO_3 (M = Li, Na, K, Rb or Cs) promoted MgO are presented in Fig. 1. The oxygen conversions (not shown in the figure) were also much higher over the latter catalysts than the former one (65–74 mol% vs 52–55 mol%). The main products over all the catalysts are ethane, ethylene, carbon dioxide, carbon monoxide, and water, the latter being separated from the products and not analyzed.

It is evident from Fig. 1 that over the pure MgO, the methane conversion (6.0 mol%), C_2 selectivity (30.0 mol%), and C_2 yield (1.8%) are quite low, the carbon oxides being selectively produced. This is consistent with the previous findings (*1*, *27*). Some of the pure alkali metal compounds also exhibited a similar low performance. Since the melting points of these alkali compounds are close to the reaction temperature, the unsupported systems were not studied further.

Monoalkali-Promoted MgO

When 10 mol% alkali compound was deposited on MgO followed by its calcination, both the methane and oxygen conversions, C_2 selectivities and, hence, C_2 yields increased to some extent (Fig. 1). However, the carbon oxides still dominated the products and varied slightly depending on the nature of the alkali compounds. Among the alkali compounds, the Li compound(s) (acetate, hydroxide, carbonate, or nitrate) promoted MgO exhibited the highest performance; for chlorides the highest performance was exhibited by NaCl. The Rb-compound-promoted MgO was the least effective. Depending on the nature of the anion associated with the alkali cation, the C_2 yield varied between 4.2 and 5.5% over

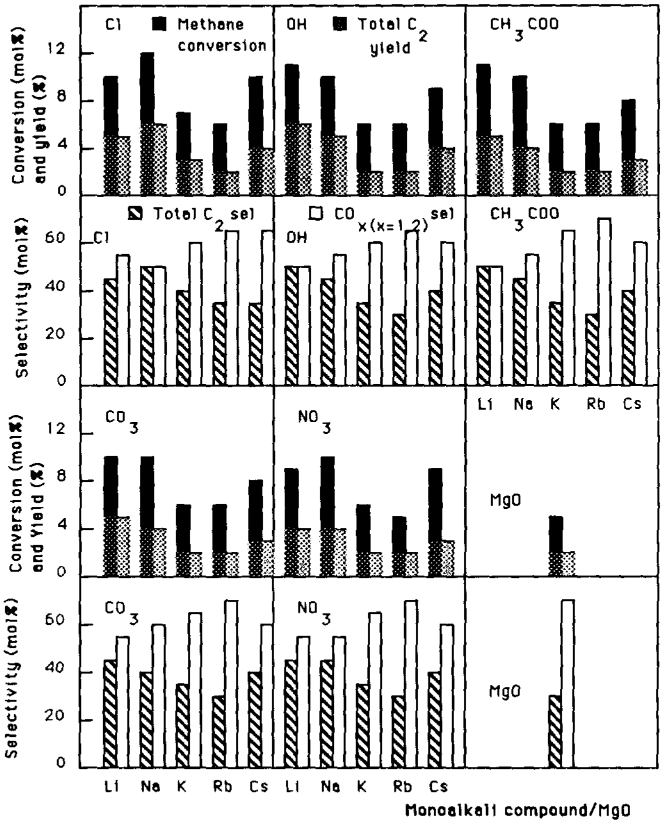

FIG. 1. The methane conversion, selectivity, and C_2 yield of the oxidative coupling of methane over the 10 mol% monoalkali-metal-compound-promoted magnesia. Reaction conditions: temperature, 750°C; atmospheric pressure; $P_{CH_4} = 608$ Torr; $CH_4/O_2 = 4$; space velocity, 15,000 $cm^3\ g^{-1}\ h^{-1}$; catalyst, 0.2 g. The products are measured after 1 h of reaction.

Li-promoted MgO and between 1.5 and 2.1% over the Rb-promoted MgO. In terms of the influence of the anions, the following sequence was observed: $Cl^- > OH^- > Ac^- > CO_3^{2-} > NO_3^-$. In general, the following sequence was observed for the cations: $Li^+ > Na^+ > Cs^+ > K^+ > Rb^+$, except for the MCl-promoted systems which showed a higher C_2 yield over the NaCl-promoted MgO than the LiCl-promoted system. The C_2 yields, however, obtained over all these monoalkali-promoted MgO are much lower than those reported by Otsuka *et al.* (*33*) over 20 mol% LiCl/MgO. This is most probably due to the extremely low partial pressures of methane and oxygen and low space velocity used by those authors, in contrast to the undiluted feed-gases and high space velocity used in the present study.

Bialkali-Promoted MgO

Upon promoting MgO with any bialkali metal compounds (total loading 10 mol%) via simultaneous impregnation with both compounds, significant increases in methane conversion and, particularly, in C_2 selectivity were observed (Fig. 2), compared to those over the respective monoalkali-promoted MgO systems. The oxygen conversion also increased to a great extent approaching 100 mol%. The catalytic performances, however, depend on the nature of the alkali compounds forming the pair.

Thus, the maximum steady-state methane conversion (23.8 mol%) and C_2 selectivity (83 mol%) with an ethylene-to-ethane molar ratio of 2.2 were obtained over (5 mol% NaCl + 5 mol% CsCl)/MgO. This gives rise to a C_2 yield of 19.7%, which is higher than or comparable to the best values for the alkali doped alkaline earth oxides, transition metal oxides, or rare earth oxides reported in literature (*1*, *6*, *8*, *18*, *19*). Similar high methane conversions and C_2 selectivities were observed over the sodium and cesium hydroxides, acetates, carbonates, or nitrates forming the promoting pair. However, the nitrate pair was the least effective, as in the monoalkali-promoted systems. In terms of the influence of the anions, the following sequence was observed: $Cl^- > OH^- > Ac^- > CO_3^{2-} > NO_3^-$, which is the same as that for the monoalkali-promoted systems (Fig. 1). The gel-precipitated MgO powder when promoted with the bialkali compounds was less effective than MgO prepared via the sol–gel process followed by its impregnation with the bialkali compounds.

Apart from $(Na^+ + Cs^+)/MgO$, only two other pairs, namely $(Li^+ + Na^+)/MgO$ and $(Li^+ + Cs^+)/MgO$, exhibited significant improvements in performance giving C_2 yields of 13.1–17.5% and 12.0–18.5%, respectively (Fig. 2). Again, the chloride-containing pairs were the most effective and the nitrate-containing ones the least effective

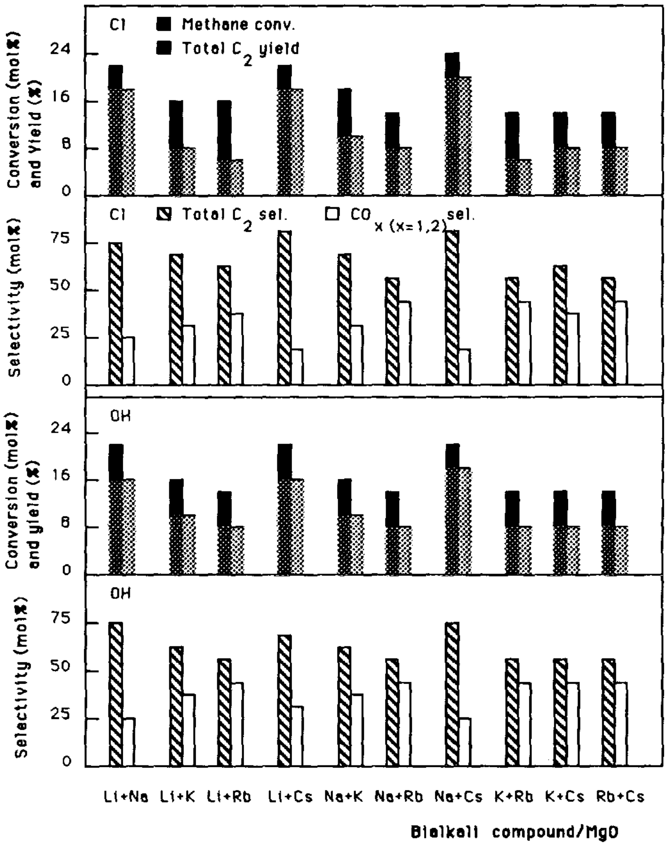

FIG. 2. The methane conversion, selectivity, and C_2 yield of the oxidative coupling of methane over the (5 mol% + 5 mol%) bialkali-metal-compound-promoted magnesia. The reaction conditions and symbols are as in Fig. 1.

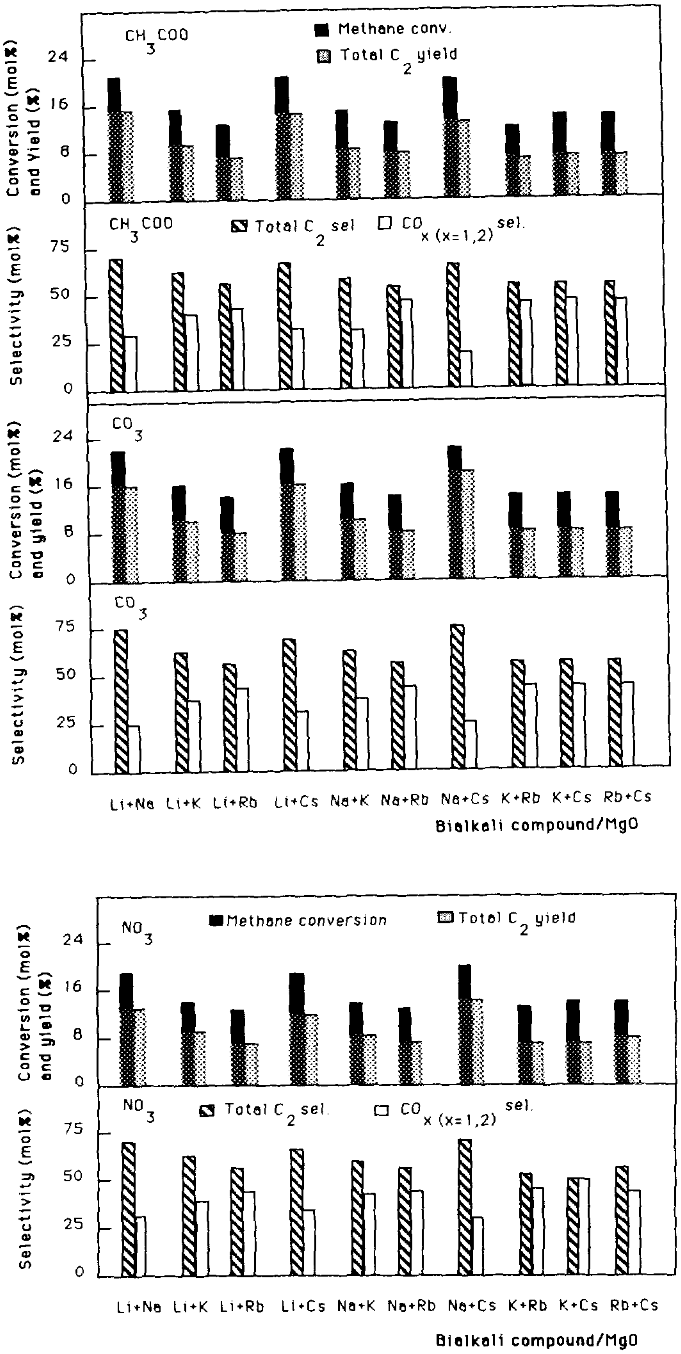

FIG. 2—*Continued*

for the same pair of cations. In contrast, the remaining seven pairs obtained from the combination of LiA (A = Cl^-, OH^-, Ac^-, CO_3^{2-}, or NO_3^-) with KA or RbA, NaA with KA or RbA, KA with RbA or CsA, and RbA with CsA were less effective than the other three systems. The C_2 yields over these systems were in the range of 6.5–9.7% only, which are half of those obtained over the best three systems. Nevertheless, these values were still much higher than those of the respective monoalkali-promoted systems for the same promoter loading (10 mol%) as that of the pair.

Effect of Alkali Loadings

Since the pairs originating from the combination of Li^+, Na^+, or Cs^+ and supported on MgO produced the most effective systems, further investigations concentrated on these promoted systems. Table 2 presents the effects of the mono- and bialkali metal chloride loadings on MgO and the catalytic behavior of the resulting catalysts. The loadings were varied from 1 to 20 mol% for the monoalkali systems, whereas the total loadings for the bialkali systems from 2 to 40 mol% with an equal molar amount of both chlorides. With the increase in alkali chloride loading, the monoalkali systems (LiCl, NaCl, or CsCl/MgO) show enhanced conversions and C_2 selectivities, the 20 mol% systems exhibiting the highest performances. However, these values are still much lower than those obtained with any bialkali-promoted sys-

TABLE 2

Effect of Mono- and Bialkali Metal Chloride Loadings on the OCM over MgO-Supported Catalysts

Catalyst	Conversion (mol%)		Selectivity (mol%)				C_2 Yield, (%)	C_2H_4/C_2H_6 molar ratio
	CH_4	O_2	C_2H_6	C_2H_4	CO_2	CO		
1% LiCl/MgO	5.5	59	12.0	27.0	51.0	10.0	2.1	2.2
5% LiCl/MgO	8.0	60	14.0	30.0	49.0	7.0	3.5	2.1
10% LiCl/MgO	10.4	68	16.0	31.0	50.0	3.0	4.0	1.9
20% LiCl/MgO	11.0	66	16.0	33.0	49.0	2.0	5.4	2.1
1% NaCl/MgO	6.7	61	14.0	28.0	52.0	6.0	2.8	2.0
5% NaCl/MgO	9.8	64	15.0	30.0	51.0	4.0	4.4	2.0
10% NaCl/MgO	12.0	65	15.0	34.0	51.0	0.0	5.9	2.3
20% NaCl/MgO	13.4	67	16.0	34.0	50.0	0.0	6.7	2.1
1% CsCl/MgO	6.0	65	17.0	19.0	58.0	8.0	2.2	1.1
5% CsCl/MgO	8.5	68	18.0	22.0	56.0	6.0	3.2	1.1
10% CsCl/MgO	10.2	70	18.0	22.0	56.0	4.0	4.1	1.2
20% CsCl/MgO	11.2	71	19.0	23.0	50.0	8.0	4.7	1.2
1% LiCl+ 1% NaCl/MgO	12.8	70	22.0	46.0	30.0	2.0	8.7	2.1
5% LiCl+ 5% NaCl/MgO	22.4	82	27.0	51.0	22.0	0.0	17.5	1.9
10% LiCl+10% NaCl/MgO	21.5	85	28.0	52.0	20.0	0.0	17.2	1.9
20% LiCl+20% NaCl/MgO	19.0	86	22.0	39.0	35.0	4.0	11.6	1.8
1% LiCl+ 1% CsCl/MgO	13.2	72	20.0	49.0	28.0	3.0	9.1	2.5
5% LiCl+ 5% CsCl/MgO	22.8	85	28.0	53.0	19.0	0.0	18.5	1.9
10% LiCl+10% CsCl/MgO	22.0	86	27.0	52.0	20.0	1.0	17.4	1.9
20% LiCl+20% CsCl/MgO	19.2	88	21.0	42.0	32.0	5.0	12.1	2.0
1% NaCl+ 1% CsCl/MgO	14.5	71	23.0	44.0	30.0	3.0	9.7	1.9
5% NaCl+ 5% CsCl/MgO	23.6	85	26.0	57.0	17.0	0.0	19.6	2.2
10% NaCl+10% CsCl/MgO	24.8	88	25.0	55.0	20.0	0.0	19.8	2.2
20% NaCl+20% CsCl/MgO	20.0	90	21.0	43.0	33.0	4.0	12.8	2.1

Reaction conditions: temperature = 750°C; pressure = atmospheric; space velocity = 15,000 $cm^3 g^{-1} h^{-1}$; P_{CH_4} = 608 Torr; $CH_4/O_2 = 4$; catalyst, 0.2 g. The results are after 1 h of reaction.

tems. For the latter, the highest performances were exhibited by the systems (10 mol% NaCl + 10 mol% CsCl)/MgO, exhibiting the highest methane conversion (24.8 mol%) and C_2 yield (19.8%). The performance of (5 mol% NaCl + 5 mol% CsCl)/MgO was very close to these values. For the other two systems (LiCl + NaCl and LiCl + CsCl), the best performances were exhibited by (5 mol% + 5 mol%)/MgO sys-

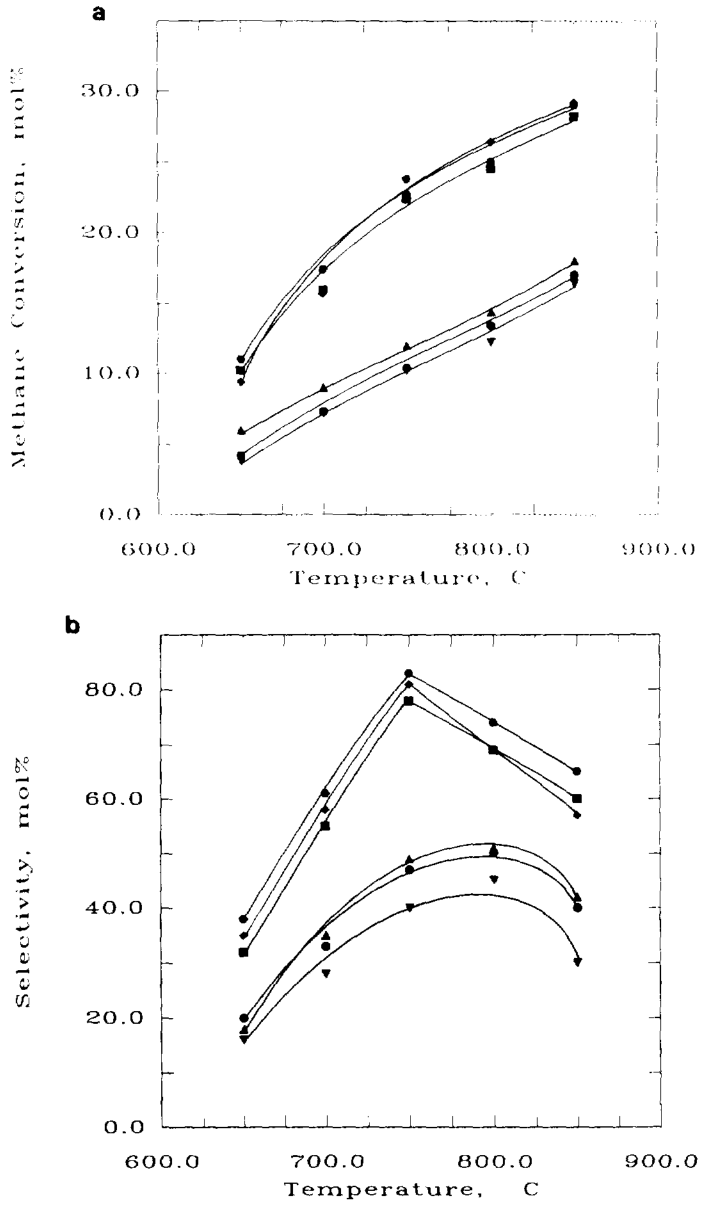

FIG. 3. The effect of reaction temperature on methane conversion (a) and C_2 selectivity (b) over mono- and bialkali-metal-chloride-promoted magnesia. The reaction conditions are as in Fig. 1, except the temperature. ●, 10 mol% LiCl/MgO; ▲, 10 mol% NaCl/MgO; ▼, 10 mol% CsCl/MgO; ■, 5 mol% LiCl + 5 mol% NaCl/MgO; ◆, 5 mol% LiCl + 5 mol% CsCl/MgO; ⬢, 5 mol% NaCl + 5 mol% CsCl/MgO.

tems. Further increases in the alkali chloride loadings (greater than 10 mol% for each) decreased the conversion and selectivity. The C_2H_4/C_2H_6 molar ratio over the bialkali-promoted systems varied between 1.8 and 2.5, which are close to those over the monoalkali-promoted systems.

Effect of Temperature and the Stability with Time-on-Stream

Figure 3 presents the temperature dependence of methane conversions and C_2 selectivities over some of the mono- and bialkali-metal-chloride-promoted MgO. For the monoalkali systems, the methane conversion grows (Fig. 3a) as the reaction temperature increases from 650 to 850°C, but the C_2 selectivity passes through a maximum (45–50 mol%) at 800°C (Fig. 3b). For the bialkali-promoted systems a similar trend is observed, except with much higher conversions, which increase up to 29 mol% at 850°C, and significantly higher C_2 selectivities, which pass through a maximum (78–83 mol%) at 750°C, than the respective monoalkali systems. The (5 mol% NaCl + 5 mol% CsCl)/MgO exhibited the highest performance at all temperatures. A similar temperature dependence pattern was observed over the mono- and bialkali-metal-hydroxide-promoted MgO, except with lower values than for the former.

The stability with time-on-stream for the bialkali-promoted systems is much higher than that for the monoalkali-promoted systems (Fig. 4). Thus, during 60 h on-stream, the C_2 selectivity over the monoalkali-promoted systems suffered a 50% loss from the initial values, the 10 mol% LiCl/MgO being the least stable one. In contrast, the bialkali-metal-chloride-promoted systems exhibited only a 10–12% loss, achieving a steady state selectivity of 70–75 mol%. Again, the (5 mol% NaCl + 5 mol% CsCl)/MgO was the most stable, with a methane conversion of 17.6 mol% and C_2 selectivity of 75 mol% after 60 h of operation.

Effect of the Pseudo-contact Time

In order to determine the effect of the reciprocal space velocity [the pseudo-contact time (W/F)], the amount of catalyst

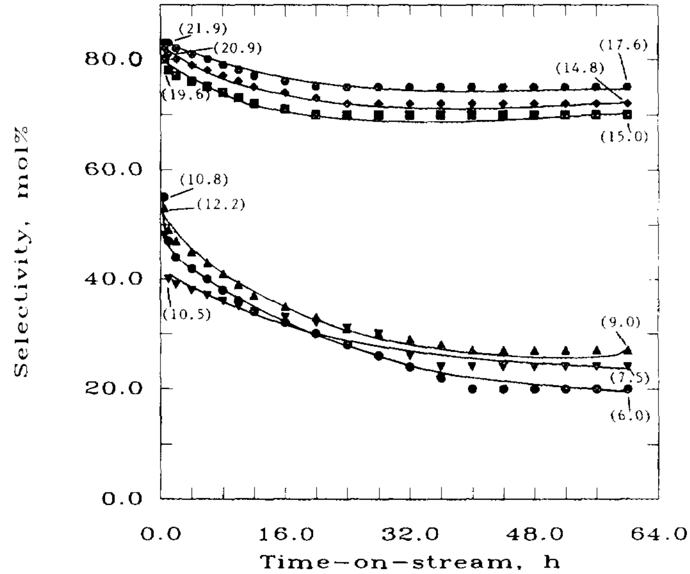

FIG. 4. The change in C_2 selectivity with time-on-stream over the mono- and bialkali-metal-chloride-promoted magnesia. The conditions are as in Fig. 1 and the symbols are as in Fig. 3. (The methane conversion values are given in parenthesis.)

(W) was varied while the flow rate (F) was held constant. Figure 5 illustrates the effect of the reciprocal space velocity over some mono- or bialkali-metal-hydroxide-promoted MgO. For the monoalkali-promoted systems, *the methane conversions in*creased initially with the increase in *W/F* from 0.06 to 3.84 g s ml^{-1} at 750°C (Fig. 5a). This increase was slightly higher over the 10 mol% LiOH/MgO than that over the 10

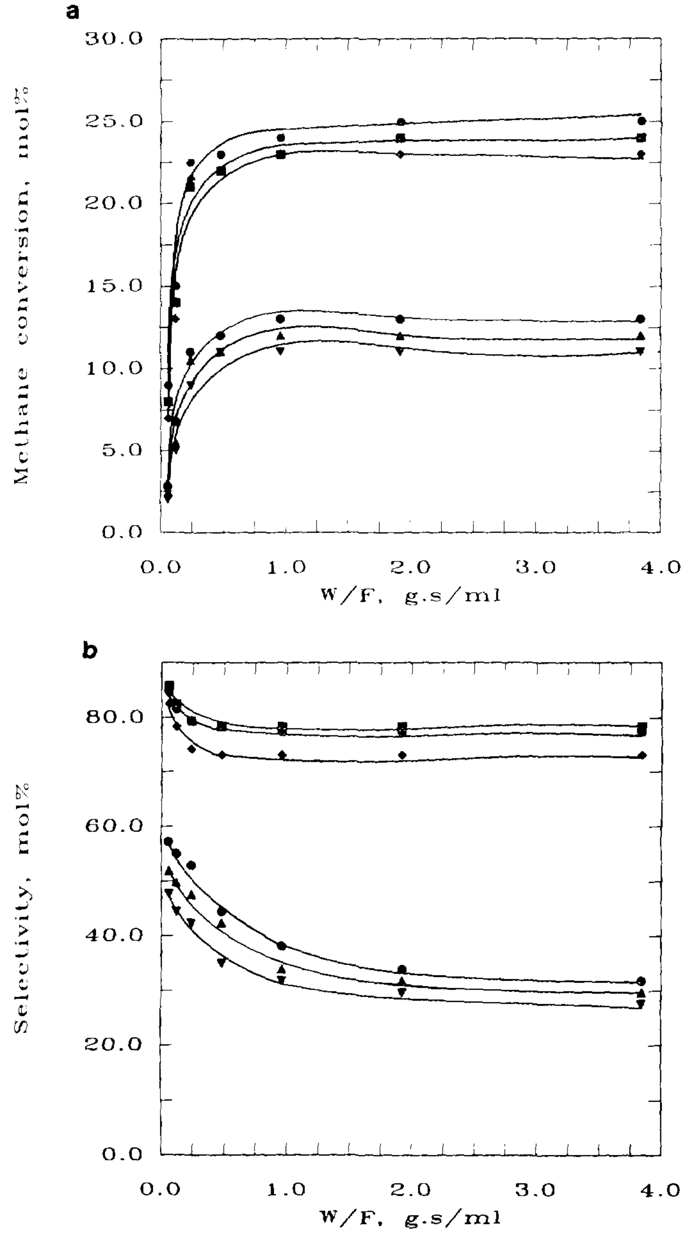

FIG. 5. The effect of pseudo-contact time (*W/F*) on methane conversion (a) and C_2 selectivity (b) over the mono- and bialkali-metal-hydroxide-promoted magnesia. The conditions are as in Fig. 1 and the symbols are as in Fig. 3.

mol% NaOH/MgO or 10 mol% CsOH/MgO. For values of W/F greater than 0.48 g s ml^{-1}, the methane conversion became independent of W/F. For the bialkali promoted systems, a similar pattern for the dependence on the pseudo-contact time was observed, except that the conversion levels were much higher than for the monoalkali-promoted systems. The C_2 selectivity for the monoalkali promoted systems decreased with increasing pseudo-contact time (Fig. 5b), the decrease being more pronounced at short contact times than at long contact times. For the bialkali-promoted systems, the C_2 selectivity decreased slightly only for short contact times (from 0.06 to 0.48 g s ml^{-1}), becoming independent thereafter. These findings are approximately consistent with those in Refs. (*27*, *34*), obtained over different catalytic systems.

Basicity and Base Strength Distribution

In an attempt to explain the difference in behavior between the mono- and bialkali-promoted MgO systems, we have measured the basicity and base strength distribution of some selected systems by the gaseous acid (CO_2) adsorption followed by its stepwise thermal desorption (STD), and by the benzoic acid titration with indicators. In the STD method any contribution from the residual chlorine released from the sample at elevated temperatures was eliminated by passing the effluent through a heptanol–liquid N_2 bath (−40°C). The basicity possessed by and the base strength distribution on the pure MgO and the mono- or bialkali-metal-chloride-promoted MgO calcined *in situ* at 850°C in a helium flow under the conditions close to those of the reaction conditions are presented in Fig. 6. In this study, the amount of CO_2 chemisorbed on the catalyst at 50°C was obtained from the amount of CO_2 desorbed from 50 to 850°C. Chemisorbed CO_2 is considered to be the amount of CO_2 retained by the presaturated catalyst after it was purged with pure helium for 30 min at 50°C. It is assumed that one site is involved in the chemisorption/desorption of one CO_2 molecule (*31*).

Each column in Fig. 6 represents the number of basic sites measured in terms of CO_2 desorbed during the corresponding temperature step. The strength of these sites is expressed in terms of the range of the desorption temperatures of CO_2. Pure MgO prepared via the sol–gel process desorbs a total of 720 μmol CO_2/g in the temperature range of 50–850°C (Fig. 6a). The maximum amount of CO_2 (250 μmol/g) is desorbed in the range of 300–500°C, indicating that its base strength is more concentrated in this region than in any other temperature region. These values are approximately consistent with the reported values (*31*, *32*). Upon promoting MgO with mono- or bialkali metal chlorides, the amounts of desorbed CO_2 significantly increased, particularly for the latter systems. Moreover, the maximum desorption is shifted to higher temperatures than for pure MgO. This indicates that both the total basicity and base strength distribution are noticeably changed, particularly for the bialkali-promoted systems.

Among the monoalkali promoted systems (Figs. 6b–6d), the 10 mol% NaCl/MgO showed the largest amount of CO_2 desorbed (1500 μmol/g) over the entire temperature range, and 250 μmol/g over the temperature range of 700–850°C, which is close to the reaction temperature. For the bialkali-promoted systems (Figs. 6e–6g), the amounts of CO_2 desorbed are twice those for the respective monoalkali-promoted systems. The largest CO_2 (2750 μmol/g) is desorbed from (5 mol% NaCl + 5 mol% CsCl)/MgO, indicating that this system possesses the highest basicity. More importantly, the basicity is quite high in the range of 700–850°C, which can be seen from the significant amount of CO_2 desorbed (500 μmol/g) in this range which is close to the reaction temperature (700–850°C).

A significant improvement in basicity of and base strength distribution on the

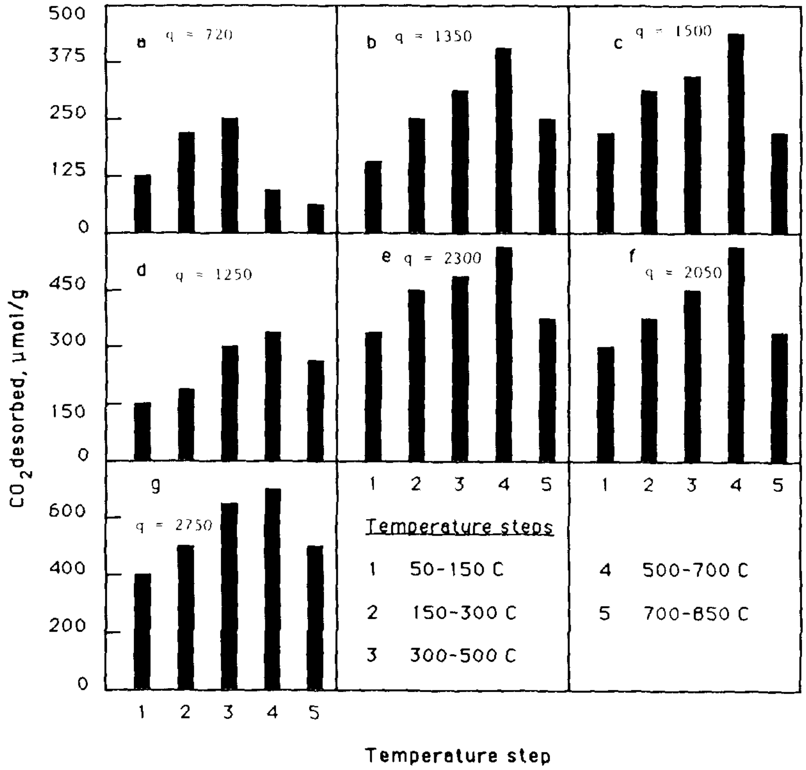

FIG. 6. Stepwise thermal desorption of pre-adsorbed CO_2 from unpromoted and mono- or bialkali-metal-chloride-promoted magnesia at 50–850°C (q = amount of CO_2 (in μmol/g) chemisorbed at 50–850°C). (a) MgO; (b) 10 mol% LiCl/MgO; (c) 10 mol% NaCl/MgO; (d) 10 mol% CsCl/MgO; (e) 5 mol% LiCl + 5 mol% NaCl/MgO; (f) 5 mol% LiCl + 5 mol% CsCl/MgO; (g) 5 mol% NaCl + 5 mol% CsCl/MgO.

bialkali-metal-chloride-promoted MgO systems compared to the monoalkali-chloride-promoted MgO or pure MgO was also observed by the conventional method of benzoic acid titration in the presence of indicators. However, it should be noted that this titration is carried out at room temperature in the presence of a solvent, i.e., under conditions different from the operating conditions of the catalyst. Moreover, this method is based on the use of indicators, and the hydrolysis of these highly basic solids due to the presence of traces of moisture makes the determination of the end-point of titration difficult (*31*). Nevertheless, the results obtained still indicate that the basicity and base strength of the bialkali-promoted MgO are significantly higher than those of the monoalkali-promoted MgO or pure MgO.

From Table 3 it is evident that only three bialkali promoted systems have an appreciable basicity in the range $26.5 \leqq H_- \leqq 35.0$ (fifth range), in addition to the noticeable basicity observed in the four previous successive ranges. In contrast, pure MgO or monoalkali-chloride-promoted MgO do not possess any basicity in the fifth range, although they show good basicity in the other four ranges. Considering the H_- values, one can conclude that the bialkali-promoted systems are superbases, in accordance with the classification of Tanabe *et al.* (*25*). It should be noted that the basicity

TABLE 3

Concentrations of Basic Ionic Sites on the Surface of Pure MgO or That Doped with Alkali Metal Chlorides as Measured by the Benzoic Acid Titration Method[a]

Sample	Concentration of basic ionic sites (mmol/g)					
	$12.2 \leq H^b \leq 15$	$15 \leq H_- \leq 17.2$	$17.2 \leq H_- \leq 18.4$	$18.4 \leq H_- \leq 26.5$	$26.5 \leq H_- \leq 35.0$	Σ
MgO	0.10	0.07	0.06	0.08	<0.01	0.31
10% LiCl/MgO	0.18	0.10	0.09	0.12	<0.01	0.49
10% NaCl/MgO	0.16	0.12	0.11	0.10	<0.01	0.49
10% CsCl/MgO	0.17	0.08	0.10	0.10	<0.01	0.45
5% LiCl+5% NaCl/MgO	0.22	0.12	0.14	0.13	0.11	0.72
5% LiCl+5% CsCl/MgO	0.21	0.11	0.15	0.13	0.12	0.72
5% NaCl+5% CsCl/MgO	0.23	0.13	0.14	0.14	0.14	0.78

[a] The accuracy of the data is 3%.

[b] H_- is the base strength determined from the pK value of an adsorbed indicator according to $H_- = pK + \log [B^-]/[BH]$, where p$K$ is the negative logarithm of dissociation constant of the indicator, [BH] is the concentration of the acidic form of the indicator, and $[B^-]$ the concentration of the basic form.

of the bialkali promoted systems measured before and after the catalytic reaction remained almost the same.

XPS Results

The electron binding energies of the elements present in the mono- or bialkali-metal-chloride-promoted MgO are in agreement with the reported values (*28*, *32*). These binding energies indicate that the alkali metal elements are in the monovalent state, as expected. The Cl*s* or Ol*s* spectra which have two different binding energies provide evidence that multiple carbon and oxygen species are present on the surface of the catalysts.

The surface compositions of the elements presented as atomic ratio of two elements are given in Table 4. In the monoalkali-promoted MgO systems (calcined, 750°C, 15 h), the Li/Mg ratio is very low, whereas

TABLE 4

Surface Composition of the Elements in Mono- and Bialkali-Metal-Chloride-Promoted MgO Determined by XPS[a]

Sample	Pretreatment/reaction conditions	Surface atomic ratio[b]				
		Li/Mg	Na/Mg	Cs/Mg	Cl/Mg	O/Mg
10% LiCl/MgO	Calcined, 750°C, 15 h	0.01	—	—	<0.01	1.8
10% NaCl/MgO	Calcined, 750°C, 15 h	—	0.08	—	<0.01	2.0
10% CsCl/MgO	Calcined, 750°C, 15 h	—	—	0.07	<0.01	2.1
5% LiCl+5% NaCl/MgO	Calcined, 750°C, 15 h	0.05	0.09	—	0.01	3.5
5% LiCl+5% NaCl/MgO	Calcined as above + OCM reaction, 750°C, 60 h	0.00	0.32	—	0.00	3.8
5% LiCl+5% CsCl/MgO	Calcined, 750°C, 15 h	0.04	—	0.08	<0.01	3.2
5% LiCl+5% CsCl/MgO	Calcined as above + OCM reaction, 750°C, 60 h	0.00	—	0.18	0.00	4.8
5% NaCl+5% CsCl/MgO	Calcined, 750°C, 15 h	—	0.072	0.081	<0.01	2.6
5% NaCl+5% CsCl/MgO	Calcined as above + OCM reaction, 750°C, 60 h	—	0.68	0.24	0.00	3.6

[a] As a reference Cl*s* = 285.0 eV was used for determining the binding energy. The precision of the data is ± 1%.

[b] Calculated from the atomic concentration determined by $C_x = (I_x/S_x)/\Sigma_i I_i/S_i)$, where I_x = relative peak area of photoelectrons from element x and S_x = atomic sensitivity factor.

those of Na/Mg or Cs/Mg are close to the loading values, although the surface Mg concentration is the same in these three systems. Evidently, a significant amount of surface Li is lost during calcination because of its high volatility, unlike the surface Na or Cs. The surface Cl concentration is also very low in all these systems, as expected. In contrast, the bialkali-chloride-promoted MgO systems (calcined, 750°C, 15 h) showed higher Na or Cs surface concentrations than those corresponding to their loadings. The surface Li in the bialkali-promoted MgO was also somewhat higher than that in the monoalkali-promoted MgO, and equal or slightly less than the loading value.

Significantly, the total surface concentration of the alkali elements in the calcined bialkali-promoted systems was twice as high than that in the respective monoalkali-promoted systems for the same total molar loading. After 60 h of catalytic reaction, the surface concentration of Na and Cs, particularly of Na, in (5 mol% NaCl + 5 mol% CsCl)/MgO significantly increased. However, the surface Li in the other two systems completely disappeared, unlike Na or Cs which showed noticeable increases after reaction. The disappearance of Li during calcination and catalytic reaction was also observed previously (*32*).

DISCUSSION

Catalytic Performance

The present work demonstrates that the impregnation of MgO (prepared via the sol–gel process) with bialkali metal compounds results in more active and stable with time-on-stream catalysts, capable of more selectively converting methane into C_2 hydrocarbons than the respective mono-alkali-compound-promoted systems or the unpromoted MgO. Depending upon the nature of the promoter compounds forming the pair, the concentrations of the alkali compounds and the appropriate reaction conditions, a significant improvement in C_2 hydrocarbons yield is obtained, which remains almost unchanged for a period of 60 h. The most effective catalytic systems, however, are obtained upon promoting MgO with the bialkali metal compounds of LiA + NaA (A = Cl^-, OH^-, Ac^-, CO_3^{2-}, or NO_3^-), LiA + CsA or NaA + CsA containing an appropriate alkali compound loading (total 10 mol%) at 750°C. This indicates that the nature of the alkali compounds forming the pair, the surface concentration of the alkali ions and the appropriate reaction conditions are the key factors in determining the catalytic behavior of the promoted MgO. In addition, the choice of a proper MgO (in this case it was prepared via a sol-gel process) has a large effect on the performance of the resulting catalysts.

The promoter effect of LiA + NaA, LiA + CsA or NaA + CsA on MgO is synergistic, since individually none of these alkali exhibits such large performances. The difference in performance is clearly not a result of the surface area, because it was the lowest (6–7 m^2/g) for the bialkali-promoted MgO systems (Table 1). Attempts were also made to evaluate some of the bialkali compounds supported on a high-surface-area MgO (160 m^2/g) obtained commercially, but the resulting materials were less effective.

The observation that out of the total 10 bialkali pairs (from any of the five anions) promoted MgO, only three systems (LiA + NaA, LiA + CsA or NaA + CsA) exhibited significant performances indicates that the nature of the cations forming the pairs exerts a greater influence than the anions associated with the cations. This is further strengthened by the finding that these three pairs originating even from the least active anion, the nitrate precursors, show quite appreciable C_2 yields (12.0–13.0%). While the anion plays a part, its role is secondary, in fact, as discussed later, after calcination the alkali compounds are converted into the corresponding oxides.

Effect of the Loadings and the Operating Conditions

The observation that the best performances are exhibited by the bialkali-chloride-promoted systems containing 5 or 10 mol% (Table 2) loading of each (total loadings 10 or 20 mol%, respectively) indicates that such loadings are sufficient to generate active surfaces for the OCM process. Further increases in the bialkali chloride loading decreases the performance, presumably because a too large fraction of the MgO is covered. It is important to note the striking differences exhibited by the mono- and bialkali-promoted MgO systems, the latter having much better performance than the former at any comparable loading.

The effect of the operating conditions (temperature and pseudo-contact time) on the performance of the mono- and bialkali-promoted MgO systems may allow to identify the possible routes for C_2 hydrocarbons and carbon oxides formations. The increase in the methane conversion and C_2 selectivity with the reaction temperature over both the mono- or bialkali-promoted systems (Figs. 3a and 3b) suggests that the formation of the reactive intermediates (methyl radicals, which are generally considered as the active species) by the catalysts is facilitated by high temperatures (>700°C). The total C_2 selectivity passes through a maximum at 800 and 750°C for mono- and bialkali-promoted systems, respectively, which suggests that the oxidation of methane and, possibly, of the C_2 products to carbon oxides is facilitated by high temperatures.

The effect of the pseudo-contact time indicates whether the C_2 hydrocarbons and the carbon oxides are formed via the same route or via parallel routes. The formation of both C_2 hydrocarbons and carbon oxides, although the latter with much lower selectivity over the bialkali-promoted systems than over the monoalkali promoted ones, at a short pseudo-contact time (Fig. 4b) is indicative of the existence of two parallel routes: one which leads to C_2 hydrocarbons and the other to carbon oxides, as already noted for other catalysts (*35, 36*). The decrease in total C_2 selectivity with increasing pseudo-contact time for the monoalkali-promoted systems and the relatively small decrease until 0.48 g s ml^{-1} followed by its independence of W/F for the bialkali-promoted systems indicates that at longer residence times in the monoalkali-promoted catalyst beds methane is more likely to be oxidized than to be coupled, unlike the bialkali-promoted systems. Presumably, the intrinsic properties of the bialkali-promoted systems make them less prone to be oxidized even at longer residence times than the monoalkali-promoted systems. In spite of the initial decrease in the C_2 selectivity with the pseudo-contact time (up to $W/F = 0.48$ g s ml^{-1}), the total C_2 yield increases noticeably and then remains almost unchanged because the increase in methane conversion over the bialkali-promoted systems compensates for the further oxidation of the C_2 molecules formed. In contrast, the monoalkali-promoted systems continue to exhibit a decreasing C_2 yield. This implies that, although the mechanism of C_2 hydrocarbons formation over the monoalkali- and bialkali-promoted systems is apparently the same, the latter exhibits much better performance than the former due to some intrinsic properties.

It is generally accepted that the generation of methyl radicals from methane by reactive oxygen species (O^- and/or O^{2-}) of the oxide catalysts is a crucial step in the OCM process (*1, 35, 36*). These methyl radicals recombine to form C_2 hydrocarbons and are also oxidized to form carbon oxides. The active sites for abstracting hydrogen from methane are presumably generated in larger numbers over the bialkali promoted catalysts than the monoalkali promoted ones. This gives rise to the enhanced performance observed for the bialkali-promoted catalysts. The high ethylene-to-ethane ratio observed over the catalysts originating from chloride precursors can be related to the influence of chlorine species, in addition to that of the bialkali metal ions. The noticeable enhancement of ethylene-to-ethane ratio in the presence of chlorine species has been observed by many researchers (*27*, *33*, *34*, *37*). The alkali compound promoters originating from CO_3^{2-}, Ac^-, NO_3^- precursors are converted to their respective oxides after calcination. Their lower performance can be explained at least in part by the absence of the active species like chlorine.

Influence of the Basicity and Surface Concentration of Alkali

A major finding of the present study is that those bialkali-promoted systems that exhibit significant catalytic performances possess also high basicity, and are even superbasic in nature. Although the striking differences observed between the mono- and the bialkali-promoted MgO or among the various bialkali-promoted MgO systems could not be fully elucidated, it is evident that the systems possessing a higher basicity exhibit higher performances.

Indeed, high basicity and high base strength were observed in three calcined catalysts: (5 mol% LiCl + 5 mol% NaCl)/MgO, (5 mol% LiCl + 5 mol% CsCl)/MgO, and (5 mol% NaCl + 5 mol% CsCl)/MgO (Fig. 6 and Table 3). Because of their high basicity and base strength distribution, these three catalysts can be considered as superbases, as already noted in the Results section. The XPS results revealed that after 60 h of catalytic reaction the surface concentration of the alkali elements (Na and Cs) is much higher in the bialkali-promoted systems than in the respective monoalkali-promoted systems, for the same total molar loading. The (5 mol% NaCl + 5 mol% CsCl)/MgO system, which possesses the highest superbasicity after calcination, also shows the highest surface concentration of the alkali atoms after calcination and even a higher one after reaction (Table 4). It is likely that the formation of high basicity is related to the high surface concentration of the alkali elements. The high concentrations on the surface are probably due to the enrichment of the surface with the alkali elements, enrichment stimulated by the decrease in the free energy of the system. Such enrichment does not occur to the same extent in the monoalkali-promoted systems. Our experiments demonstrate that the enrichment is strongly stimulated by the presence of a second alkali. After the catalytic run, the above system exhibited a very high enrichment with Na and to some extent with Cs. However, the basicity of the bialkali promoted MgO measured by CO_2 desorption (STD method) remained almost the same before and after the catalytic reaction. This explains why, over the bialkali promoted systems, the conversion and selectivity changed little with time. There is no contradiction between the XPS and the STD results, since XPS detects the surface concentration in a layer of about 10 nm, while the STD method involves only the outermost layers.

The somewhat lower performance and stability of the other two systems (5 mol% LiCl + 5 mol% NaCl)/MgO and (5 mol% LiCl + 5 mol% CsCl)/MgO could be attributed to the loss of the surface Li during the calcination and also during the reaction. It appears that the alkali ions whose ionic radii are very different, such as Na + Cs or Li + Cs, are most effective. This probably occurs because it is more likely for small ions to find free space on the surface among the large ions and thus the surface to become more fully occupied. As a result, the surface free energy is much more decreased.

CONCLUSIONS

The following conclusions can be drawn from the present study on the effect of superbasic catalysts on the OCM process:

(1) The catalytic performances of a number of solid superbasic materials prepared by promoting MgO with bialkali metal com-

pounds have been evaluated for the OCM reaction. A comparison of these performances with those of the respective monoalkali-promoted systems reveal that the former systems are significantly more effective than the latter.

(2) The bialkali-metal-promoted systems originating from the lithium with sodium or cesium, and sodium with cesium compounds (Cl^-, OH^-, Ac^-, CO_3^{2-}, or NO_3^-) produce effective systems, unlike the systems containing potassium- or rubidium compounds. The most effective compounds were those originating from Cl^- or OH^-.

(3) The best catalytic performance is obtained over (5 mol% NaCl + 5 mol% CsCl)/MgO and (10 mol% NaCl + 10 mol% CsCl)/MgO, which exhibit a C_2 hydrocarbon yield of 19.7–19.8% compared to 5.9 and 4.1% over 10 mol% NaCl/MgO and 10 mol% CsCl/MgO, respectively. In addition, the stability with time-on-stream over the bialkali-promoted systems is much better than with the monoalkali-promoted ones.

(4) The nature of alkali compounds forming the pair, the choice of a proper MgO, the promoter content, and the appropriate reaction conditions are key factors in determining the effectiveness of the systems.

(5) The basicity and base strength distribution of the bialkali-promoted systems that exhibit significant catalytic performances are close to those of superbasic materials, unlike the monoalkali-promoted systems. The relatively high activity, selectivity, and stability with time-on-stream over the bialkali-promoted systems are attributed to the superbasicity of the resulting catalysts. The superbasicity of bialkali-promoted systems is due to the significant enrichment of the surface of the catalyst with the alkali ions, the presence of a second alkali enhancing the enrichment.

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