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Synergistic effect of bialkali metal chlorides promoted magnesia on oxidative coupling of methane

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Upon promoting MgO (prepared via a sol–gel process) with any binary mixture of the alkali metal chlorides, catalytic systems are obtained which are more active, selective and much more stable with time-on-stream than the respective monoalkali promoted MgO in the oxidative coupling of methane (OCM) to C_2 hydrocarbons. The best catalytic performance is obtained over (5 mol% NaCl+5 mol% CsCl)/MgO, which exhibits a C_2 yield of 19.7% compared to 5.9 and 4.1% over 10 mol% NaCl/MgO and 10 mol% CsCl/MgO, respectively, at atmospheric pressure, a temperature of 750°C, a space velocity of 15000 $\text{cm}^3\ \text{g}^{-1}\ \text{h}^{-1}$, $P_{CH_4} = 608$ Torr and $CH_4/O_2 = 4$. A series of different combinations among the five alkali chlorides were made and the afore-mentioned synergistic effect was always observed. The basicity and base strength distribution of the bialkali chloride systems (measured by the gaseous acid adsorption or benzoic acid titration methods) are significantly higher than those of the respective monoalkali halide systems. The relationship between the catalytic performance and basicity/base strength distribution is explored.

Keywords: Methane; oxidative coupling; bialkali promoted magnesia

1. Introduction

Solid materials possessing an appreciable surface basicity are suitable catalysts for the oxidative coupling of methane (OCM) to C_2 hydrocarbons at temperatures higher than 700°C and atmospheric pressure [1–3]. It has been reported [4] that the C_2 selectivity and the basicity of the alkaline earth metal oxides are in the order: $BeO < MgO < CaO < SrO < BaO$. When MgO is doped with NaOH, the resulting material exhibits enhanced basicity, which in turn increases the C_2 selectivity of methane coupling [3]. This indicates that the basic sites are beneficial for the selective formation of C_2 hydrocarbons and that by a proper combination of an alkaline earth oxide with an alkali metal salt an increased basicity can be obtained. A num-

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ber of researchers [5–10] have investigated the relationship between the surface basicity and the C_2 selectivity. Although the nature of the solid catalyst, the method of basicity enhancement, the methods of measurement of basicity and base strength distribution and their values varied greatly, the essence of all these investigations was the same: there exists a direct correlation between basicity and the C_2 selectivity; the latter increases as the former is enhanced.

This suggests that increasing the basicity of the system one can increase the activity and selectivity for C_2 of the catalyst. We observed that enhanced basicity can be achieved by using as promoter a binary mixture of alkali metal compounds rather than individual compounds. The observation that the basicity can be increased to significantly higher values (superbasic) when a binary mixture of the alkali metals is employed rather than the single metal was first made by Malinowski et al. [11]. It will be shown in what follows that, if MgO is promoted with two alkali metal compounds instead of one, superbasic catalysts are obtained which are more active, more selective for C_2 and more stable with time- on-stream than the systems promoted with single alkali metal compounds.

2. Experimental

2.1. CATALYST PREPARATION

MgO was prepared by a sol–gel method [12]. The method involves the hydrolysis of magnesium ethoxide dissolved in ethanol in the presence of an acid catalyst (HCl, pH = 3) with 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. This MgO powder was impregnated with mono- or bialkali metal chloride(s) by introducing an aqueous solution of the alkali metal salt(s) into an aqueous slurry of MgO with stirring at 80°C. This was 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.

2.2. CATALYST SCREENING AND PRODUCT ANALYSIS

The methane coupling reactions were performed at 650– 850°C, under atmospheric pressure, by co-feeding 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 set-up have been published previously [13]. 200 mg of catalyst sandwiched between quartz wool plugs were placed in the center of the tube reactor. The flow of each gas (99.99% purity) was controlled by a variable constant differential flow controller, the total flow rate being 50 ml/min (NTP). Under these conditions the empty reactor produced less than 0.5% conversion of methane.

The reaction products, after being separated from water, were sampled on-line using an automatic 10-port sampling valve, and analyzed by a gas chromatograph (PE Sigma 2000) fitted with two detectors (thermal conductivity and flame ionization detectors) and three columns: a molecular sieve 5A, a Porapak T and a Chromosorb 102 (all 6 ft × 1/8 in). The response factors for the reactants and products were determined using certified calibration gases (Cryogenic Supply). The surface areas of the calcined and post-catalysis samples were measured by the BET method and the values were in the range 10–20 m^2/g.

2.3. BASICITY/BASE STRENGTH DISTRIBUTION MEASUREMENT

The basicity and base strength distribution of the solid catalysts were determined by the benzoic acid titration method using indicators [14], and by the gaseous acid (CO_2) adsorption followed by its stepwise thermal desorption (STD) [15,16]. In the STD method, high purity CO_2 (99.995%) was chemisorbed on the calcined (in situ) catalyst at 50°C followed by the degassing at 50°C of the physically adsorbed CO_2 in a flow of helium and finally by the heating from 50 to 850°C in a number of successive steps (50–150, 150–300, 300–500, 500–700 and 700–850°C). The amount of CO_2 desorbed in each step was determined using a thermal conductivity detector suitably calibrated.

3. Results and discussion

The main products of OCM over pure MgO, and on mono- or bialkali metal chloride(s) promoted MgO are ethane, ethylene, carbon dioxide, carbon monoxide and water, the latter being separated from the products and not analyzed. The results obtained at 750°C after 1 h of reaction over various catalysts are presented in table 1. 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.

For the pure MgO, the methane conversion and C_2 selectivity are quite low, the carbon oxides being selectively produced (table 1). The pure MCl (M = Li, Na, K, Rb or Cs) also showed a similar low activity and selectivity.

When 10 mol% MCl was deposited on MgO, both the methane conversions and C_2 selectivities increased to some extent, but carbon oxides still dominated the products. In terms of the catalytic performance, the following sequence was observed: NaCl > LiCl > CsCl > KCl > RbCl. The C_2 yield, obtained over these catalysts, is much lower than that reported by Otsuka et al. [17] for LiCl/MgO. This is possibly due to the extremely low partial pressures of methane and oxygen and

Table 1
Oxidative coupling of methane over mono- and bialkali metal chlorides promoted MgO. Reaction conditions: temperature = 750°C, pressure = atmospheric, P_{CH_4} = 608 Torr, space velocity = 15000 $cm^3\ g^{-1}\ h^{-1}$, $CH_4/O_2 = 4$, catalyst = 0.2 g; results are after 1 h of reaction

Catalyst[a]	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		
MgO	5.8	52	21.0	8.0	58.0	13.0	1.5	0.3
10% LiCl/MgO	10.4	68	16.0	31.0	50.0	3.0	4.9	1.9
10% NaCl/MgO	12.0	65	15.0	34.0	51.0	0.0	5.9	2.3
10% KCl/MgO	7.0	64	18.0	20.0	57.0	5.0	2.7	1.1
10% RbCl/MgO	6.0	65	14.0	21.0	55.0	10.0	2.1	1.5
10% CsCl/MgO	10.2	70	18.0	22.0	56.0	4.0	4.1	1.2
(5% LiCl + 5% NaCl)/MgO	22.4	82	27.0	51.0	22.0	0.0	17.5	1.9
(5% LiCl + 5% KCl)/MgO	16.0	81	25.0	43.0	30.0	2.0	8.8	1.7
(5% LiCl + 5% RbCl)/MgO	14.2	82	21.0	39.0	36.0	4.0	7.3	1.8
(5% LiCl + 5% CsCl)/MgO	22.8	85	28.0	53.0	19.0	0.0	18.5	1.9
(5% NaCl + 5% KCl)/MgO	17.0	80	22.0	43.0	31.0	4.0	9.7	1.9
(5% NaCl + 5% RbCl)/MgO	14.2	84	20.0	37.0	38.0	5.0	7.5	1.8
(5% NaCl + 5% CsCl)/MgO	23.8	85	26.0	57.0	17.0	0.0	19.7	2.2
(5% KCl + 5% RbCl)/MgO	14.5	80	19.0	37.0	35.0	9.0	6.4	1.9
(5% KCl + 5% CsCl)/MgO	14.6	85	19.0	40.0	37.0	4.0	8.6	2.1
(5% RbCl + 5% CsCl)/MgO	14.0	84	18.0	39.0	36.0	7.0	8.0	2.2

[a] Loading is in mol%.

different space velocity used by those authors, in contrast to the undiluted feed-gases in the present study.

When any two alkali chlorides (the total loading 10 mol%) were deposited on MgO simultaneously, a noticeable increase in methane conversion and, particularly, in C_2 selectivity was observed compared to those of the respective monochloride promoted MgO. The performance, however, depends on the nature of the alkali cations forming the pair. Thus, the maximum methane conversion (23.8 mol%) and C_2 selectivity (83 mol%) with an ethylene-to-ethane ratio of 2.2 are 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 doped alkaline-earth oxides, transition metal oxides or rare earth oxides reported in literature [3,6,7,18] and much higher than those for 10 mol% of the monoalkali based systems (table 1). The activities and C_2 selectivities of (5 mol% LiCl + 5 mol% NaCl)/

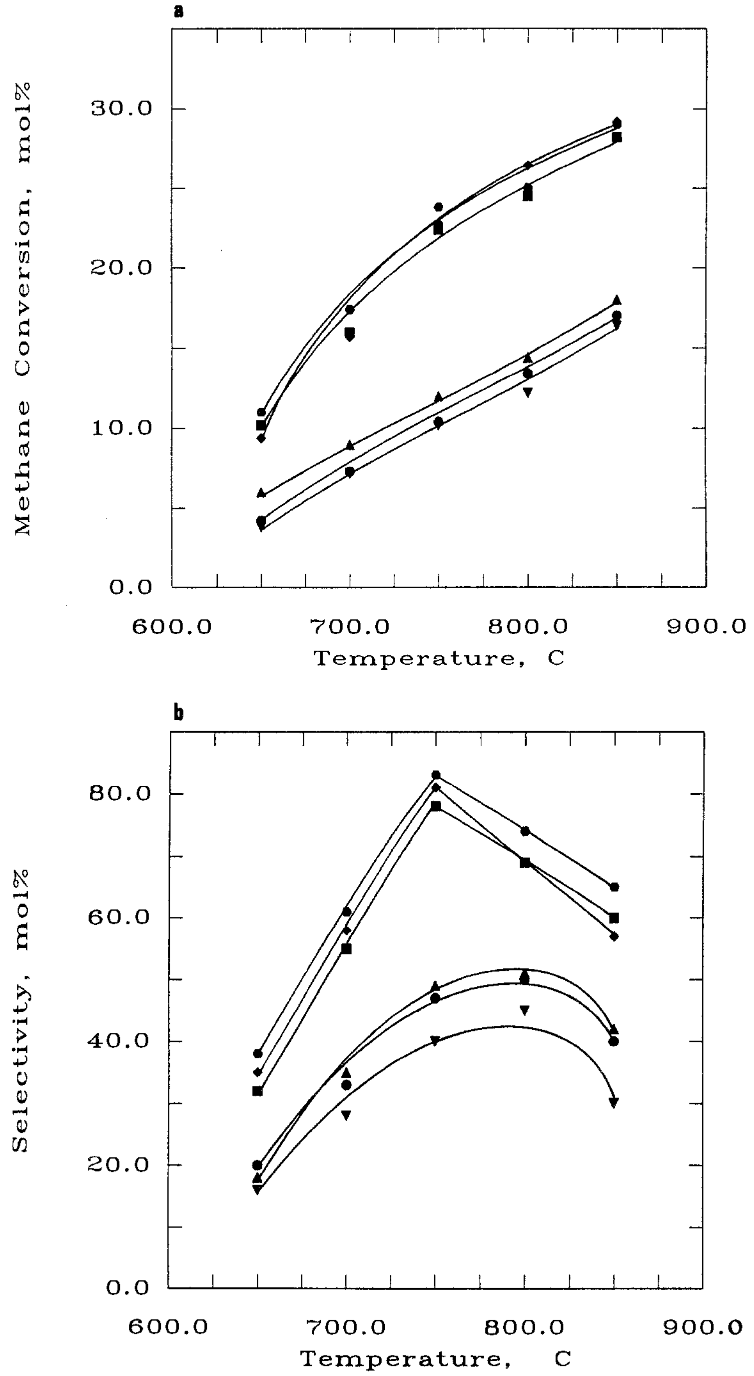

Fig. 1. The effect of reaction temperature on methane conversion (a) and C_2 selectivity (b) over mono- and bialkali metal chlorides promoted MgO. The conditions are as in table 1. (●) 10 mol% LiCl/MgO, (▲) 10 mol% NaCl/MgO, (▼) 10 mol% CsCl/MgO, (■) (5 mol% LiCl + 5 mol% NaCl)/ MgO, (◆) (5 mol% LiCl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

MgO and (5 mol% LiCl + 5 mol% CsCl)/MgO were also quite high and close to each other. In contrast, the combinations of LiCl with KCl or RbCl, NaCl with KCl or RbCl, KCl with RbCl or CsCl and RbCl with CsCl were less effective. However, their performances were still much higher than those of the respective monoalkali chloride promoted systems containing the same mol% as the total mol% of the combination.

The alkali loadings were varied from 1 to 20 mol% for the monoalkali systems, whereas the total for the bialkali systems from 2 to 40 mol% with an equal molar amount of both chlorides. With the increase in alkali chloride loadings, the monoalkali systems (LiCl, NaCl or CsCl/MgO) show enhanced conversions and C_2 selectivities, the 20 mol% systems exhibiting the highest performances in the series. But these values are still much lower than those obtained with any bialkali chloride with the same total molar loading as the monoalkali system (the results are not included in the table). The highest performances are exhibited by the systems containing 5 and 10 mol% loadings (of each chloride), and among them the (NaCl + CsCl)/MgO is the best. Further increases in the chloride loading decrease the performances, presumably, because a too large fraction of the MgO surface is covered.

Fig. 1 presents the temperature dependence of methane conversions and C_2 selectivities over some of the mono- or bialkali deposited MgO. For the monoalkali systems, the methane conversion grows (fig. 1a) as the temperature increases, but the C_2 selectivity passes through a maximum (45–50 mol%) at 800°C (fig. 1b). For the bialkali systems a similar trend is observed, except with much higher conversions (up to 29 mol%) and selectivities, the C_2 selectivity passing through a maximum (78–83 mol%) at 750°C. The stability with time-on-stream for the bialkali systems is significantly higher than that for the monoalkali systems (fig. 2). Thus, during 60 h on-stream, the C_2 selectivity over the monoalkali systems suffered a 50% loss from the initial values, the 10% LiCl/MgO being the least stable one. In contrast, the bialkali systems exhibited only a 10–12% decrease becoming stable at selectivities 70–75 mol%. The loss in methane conversion was also more pronounced for the monoalkali systems than for the bialkali ones during the same period.

In an attempt to gain an insight into the observed difference between the mono- and bialkali systems employed in the OCM process, we have measured the basicity and base strength distribution of some selected systems. The basicity and base strength distribution measured by STD of CO_2 in successive temperature steps are presented in fig. 3. Any contribution from volatile chlorine was eliminated by passing the effluent through a heptanol–liquid N_2 bath (−40°C). Each column represents the number of 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 temperature of CO_2. Evidently, pure MgO is a moderate base whose base strength is approximately consistent with the reported values [16]. Upon promoting MgO with mono- or bialkali metal chlorides, the total basicity and base strength distribution are noticeably increased, the latter exhibiting very

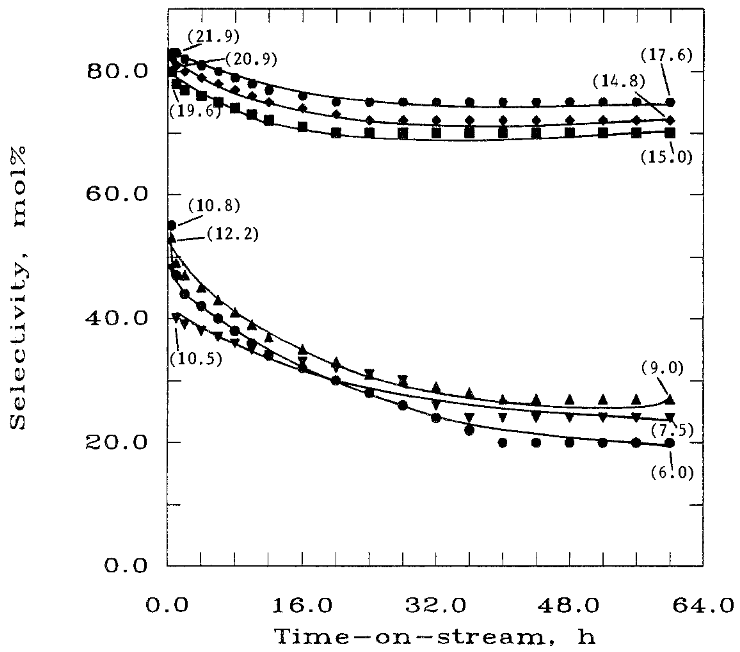

Fig. 2. The change in C_2 selectivity with time-on-stream over mono- and bialkali metal chlorides promoted MgO. The conditions are as in table 1. (The methane conversion values are given in parentheses.) (●) 10 mol% LiCl/MgO, (▲) 10 mol% NaCl/MgO, (▼) 10 mol% CsCl/MgO, (■) (5 mol% LiCl + 5 mol% NaCl)/MgO, (◆) (5 mol% LiCl + 5 mol% CsCl)/MgO, (○) (5 mol% NaCl + 5 mol% CsCl)/MgO.

large increases. Among the monoalkali-based systems, the 10 mol% NaCl/MgO system shows the largest amount of CO_2 desorbed (1500 μmol/g) over the temperature range of 50–850°C, and 250 μmol/g over the temperature range of 700–850°C, which is close to the reaction temperature. For the bialkali-based systems, the amounts of CO_2 desorbed are twice those for the respective monoalkali-based systems. The largest amount (2750 μmol/g) of CO_2 is desorbed by (5 mol% NaCl + 5 mol% CsCl)/MgO, indicating that this system possesses the highest basicity and, more importantly, the basicity is quite high (500 μmol/g) in the range of 700–850°C, which is close to the reaction temperature. The benzoic acid titration of these solids revealed that only the three bialkali-based systems have a basicity strength $H_- = \mathrm{p}K$ of the indicator in the range $26.5 \leqslant H_- \leqslant 35.0$, which indicates that they are superbase in accordance with the classification of Tanabe et al. [19].

The high basicity of the bialkali promoted MgO is probably due to the high enrichment of the surface with alkali atoms, as evidenced by our XPS measurements [20]. The surface enrichment for monoalkali promoted MgO is much lower than for bialkali. The role of the basic sites appears to be the generation of methyl radicals by abstraction of hydrogen [5–10].

Hence, the promoting of MgO with bialkali metal chlorides (LiCl, NaCl or CsCl) results in the enhancement of the basicity and has the following effects on the

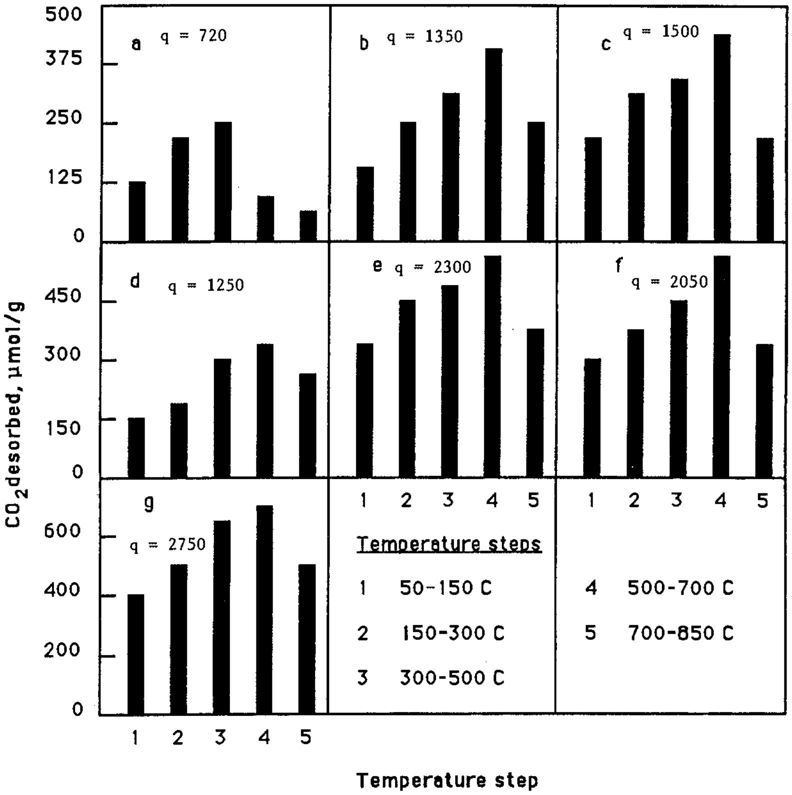

Fig. 3. Stepwise thermal desorption of CO_2 from pure or promoted MgO at 50–850°C. (q = amount of CO_2 (µmol/g) chemisorbed at 50°C). (a) MgO, (b) 10 mol% LiCl/MgO, (c) 10 mol% NaCl/MgO, (d) 10 mol% CsCl/MgO, (e) (5 mol% LiCl + 5 mol% NaCl)/MgO, (f) (5 mol% LiCl + 5 mol% CsCl)/MgO, (g) (5 mol% NaCl + 5 mol% CsCl)/MgO.

OCM process: (i) it increases the methane and oxygen conversions compared to those over the monoalkali-based MgO; (ii) it enhances the C_2 selectivity resulting in a C_2 yield of 17.5–19.7% (compared to 4.1–5.9% for monoalkali-based systems) and (iii) it significantly increases the stability of the catalyst with time-on-stream (60 h). In addition, the residual chlorine species, which are still present on the surface after calcination, as observed previously for other systems [13], are likely to contribute to the enhancement of C_2 selectivity initially.

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