JOURNAL OF CATALYSIS 143, 1–21 (1993)

Oxidative Methylation of Toluene with Methane over Superbasic Catalysts: A Selective Route to Styrene and Ethylbenzene through Alternative Feedstocks

ASHRAF Z. KHAN AND ELI RUCKENSTEIN[1]

Department of Chemical Engineering, State University of New York at Buffalo, Box 60, Buffalo, New York 14260-4200

Received February 24, 1993; revised April 22, 1993

The oxidative methylation of toluene with methane to ethylbenzene and styrene has been investigated over various monoalkali-metal-compounds-promoted MgO catalysts and superbasic catalysts prepared by promoting MgO with various binary alkali metal compounds. The experiments have been carried out under atmospheric pressure, at 650–850°C, at a $CH_4 : O_2 : C_7H_8 :$ He partial pressure ratio of 14.7 : 2.9 : 1 : 11.8 and at a space velocity of 15,000 $cm^3\ g^{-1}\ h^{-1}$. The performances of the bialkali-metal-compounds-promoted MgO are much higher than any monoalkali-promoted MgO and are found to strongly depend on the nature of the alkali metal compounds forming the pair, the concentration of the alkali metal ions, and the reaction conditions. The most effective catalytic systems are obtained with MgO promoted with the bialkali metal compounds of LiA + NaA, LiA + CsA, KA + CsA or NaA + CsA (A = SO_4^{2-}, OH^-, Cl^-, CH_3COO^-, CO_3^{2-} or NO_3^-) containing total alkali loadings of 10 mol% with equal molar amounts of both alkalis. Any bialkali-promoted system containing rubidium was less effective than those systems. The highest C_8-selectivity (57 mol%) and C_8-yield (24.2%) with a styrene/ethylbenzene molar ratio of 1.6 were obtained over (5 mol% Na^+ + 5 mol% Cs^+)/MgO (prepared from the sulfate precursors) at 750°C under the aforementioned conditions. The total C_8-selectivity and the total C_8-yield over the bialkali-promoted systems remained almost unchanged for a period of 60 h. In contrast, the maximum C_8-yield over any monoalkali-promoted system never exceeded 11.6% (styrene/ethylbenzene = 1.4) under the same conditions and the stability with time-on-stream was less prominent. The relationship between the catalytic performances and the physicochemical characteristics of the catalysts revealed by XPS and basicity measurements is explored. The relatively high performances of the bialkali-metal-compounds-promoted MgO are likely to be related to the synergistic increase in the surface basicity (superbasicity) caused by the enrichment of the surface layer with the alkali ions (Na^+ and Cs^+).

INTRODUCTION

Many research groups are conducting extensive research to replace crude oil-based chemicals with natural gas and coal-based chemicals. The latest effort is the direct conversion of methane into valuable C_2 hydrocarbons, particularly ethylene, via oxidative coupling in the presence of effective catalysts (*1*).

Currently, styrene—one of the most important industrial monomers—is produced by catalytic alkylation of benzene with ethylene over $AlCl_3$–HCl catalysts followed by oxidative dehydrogenation of the resulting ethylbenzene over potassium-promoted iron oxide catalysts (*2*). However, this process involves the utilization of benzene and ethylene, obtained from crude oil and petroleum gas, which are expensive feedstocks. In addition, the use of hazardous catalysts like $AlCl_3$–HCl constitutes an environmental concern. A different process for the production of ethylbenzene and, ultimately, styrene by oxidative methylation of toluene with methane, discovered by Khcheyan *et*

---

[1] To whom correspondence should be addressed.

0021-9517/93 $5.00

al. (*3–7*), provides an attractive route from abundant natural gas and distillates of coal tar, rather than from the limited petroleum sources, and minimizes the pollution caused by hazardous catalysts. The reaction involves the high-temperature (~700°C) interaction of methane with compounds containing a methyl group at an α-position on an electron-withdrawing functional group, such as toluene. The process proceeds with an appreciable yield in the presence of various catalysts, such as the oxides of Fe, Co, Ni, Ti, V, Bi, Mo, or Zn (*7*). However, the details regarding the catalyst compositions, method of preparation and promoter effect have not been disclosed. Yakovich *et al.* (*8*) reported that a KBr-loaded silica catalyst gives the highest selectivity to styrene and ethylbenzene, but it is not yet clear whether replacing silica with some other support would give similar results.

Recently, on the basis of catalysts used for the oxidative coupling of methane to C_2 hydrocarbons (*1, 9–11*), several groups have employed some methane coupling catalysts for the oxidative methylation of toluene with methane (*12–18*). Such studies have revealed that the oxidative methylation of toluene is catalyzed by alkali-promoted basic oxides, such as alkali/alkaline earth metal oxides, alkali/transition metal oxides, and alkali/rare earth metal oxides, which are active in the oxidative coupling of methane as well. The alkali-promoted basic oxides provide the active sites for the formation of reactive intermediates like methyl radicals and benzyl radicals by the abstraction of hydrogen from methane and toluene, respectively (*7, 17, 18*). The combination of the radicals leads to the formation of C_8 hydrocarbons (ethylbenzene and styrene) and other higher hydrocarbons. However, the catalysts thus far reported suffer from low selectivities toward the desired products and low stability with time-on-stream.

We recently reported (*19*) that a substantial synergistic effect is obtained in the oxidative coupling of methane by using various bialkali-metal-compounds-promoted magnesia, instead of monoalkali-promoted magnesia. We attributed this synergistic effect to the much higher enrichment of the surface layer with alkali ions for the bialkali- than for monoalkali-promoted magnesia. This high enrichment generates superbasic catalysts.

According to Kijenskii and Malinowskii (*20, 21*), the term "superbase" is used to denote a base strong enough to detach a proton from hydrocarbon molecules, such as triphenylmethane (pK_a of acid indicator $= 33$) or methane ($pK_a = 40$). The base strength (denoted $H_- \cong pK_a$) of a superbase should therefore lie in the range $40 \geqq H_- \geqq 33$. More recently Tanabe *et al.* (*22*) suggested that materials which possess basic sites in the range $35.0 \geqq H_- \geqq 26.5$ could be termed superbases. The latter definition is in conformity with that of solid superacids. A superbase can be obtained by promoting an oxide, such as MgO or Al_2O_3, with bialkali metals (*20*). The catalytic activity of such superbases was extremely high in the dehydrogenation of isopropylbenzene.

It is the concept of superbasic materials that prompted us to investigate their catalytic influence on the oxidative methylation of toluene with methane, since we already observed a noticeable synergistic effect of such materials on the oxidative coupling of methane (*19, 23*). In the present paper, we show that such superbasic materials are more effective in the oxidative methylation of toluene than any monoalkali-metal-compound-promoted materials. We report on a substantial synergistic effect for both the basicity as well as for the activity, C_8-selectivity, and stability with time-on-stream when binary mixtures of alkali compounds are employed as promoters, instead of the respective monoalkali compounds. Some preliminary results have been reported in a short communication (*24*).

EXPERIMENTAL

Catalyst Preparation

Pure MgO was either prepared by a sol–gel method or obtained commercially (Aldrich). The details of the catalyst preparation have been reported in Ref. (*23*). Briefly, first MgO was prepared by a sol–gel method, according to the procedure described in the literature (*25*), followed by its calcination at 900°C for 15 h, cooling to room temperature, pressing, crushing, and sieving to 60–80 mesh particle sizes. Onto this calcined MgO powder, mono- or bialkali metal compounds were deposited by the conventional impregnation method, using one of six different alkali precursors (M_2SO_4, MOH, MCl, M_2CO_3, MNO_3, or CH_3COOM, where M = Li, Na, K, Rb, or Cs). For the deposition of the monoalkali metal compound(s), an aqueous solution of the alkali metal salt(s) 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 the bialkali metal compounds, an aqueous solution of the two respective alkali metal salts prepared by dissolving the salts simultaneously in distilled water was used. The initial alkali metal loading was usually 10 mol% for the monoalkali deposition. For the bialkali metal compound deposition, the total alkali metal loading was also 10 mol%, with an equal molar amount of both compounds, except when the effect of the alkali loading was studied. Unless otherwise stated, MgO (s–g) prepared by the sol–gel method was used in all the experiments. No significant differences in the catalytic performance were observed when MgO (s–g) or that obtained commercially was employed as supports.

Reactor Setup/Catalyst Screening

A schematic diagram of the reactor setup is presented in Fig. 1. The catalytic runs were carried out in the temperature range 650–800°C, under atmospheric pressure, in a fixed-bed flow reactor constructed from a high-purity alumina tube (6 mm i.d., 30 cm long) mounted horizontally and heated by a programmable single-zone electric furnace (Lindberg 54S-142) with a built-in thermocouple. The hot zone was 8 cm long. Usually 200 mg of calcined catalyst sandwiched between quartz wool plugs was placed in the center of the reactor tube, which was connected to the gas inlet and outlet systems through Cajon fittings containing high-temperature (250°C) O-ring seals. The reactant gas mixture of high-purity methane, oxygen, and helium (all 99.9% purity; Cryogenic Supply) was passed through a toluene (99.9% purity; Aldrich) vapor saturator made of galvanized metal and maintained usually at 22°C just before the inlet of the reactor. The total flow rate of the gas mixture measured at the outlet of the reactor was 50 ml/min (NTP), which gave rise to partial pressure ratios of $P_{CH_4}:P_{O_2}:P_{C_7H_8}:P_{He}$ = 14.7 : 2.9 : 1 : 11.8. The flow of each gas was controlled by a variable constant differential flow controller (Porter VCD 1000) connected to a filter (Nupro, 7 μm) and a check valve. The reactor tube was periodically cleaned with nitric acid to eliminate the carbonaceous and alkali materials deposited on the inside wall.

Product Analysis

The gaseous products, after separated from condensed products by passing through a heptanol–liquid nitrogen bath (−40°C), were sampled on-line using an automatic 10 port-sampling valve (Valco) and analyzed by gas chromatography (Perkin–Elmer Sigma 2000) fitted with thermal conductivity and flame ionization detectors and attached to a PE 3600 data station. The GC contained a Chromosorb 102 column (3.20 mm × 1.82 m) and a Bentone 34 column (3.20 mm × 1.82 m). The condensed products were analyzed off-line by a GC/MS (Hewlett–Packard 5890 Series II) fitted with a mass-selective detector (MSD 5971A) and three columns: a molecular sieve 5A (3.20 mm × 1.82 m), a poraplot wide bore capillary (0.53 mm × 27.5 m), and a cross-linked methyl silicon capillary (0.20 mm × 12.5 m). Argon was used as an internal standard. The conversion of toluene is ex-

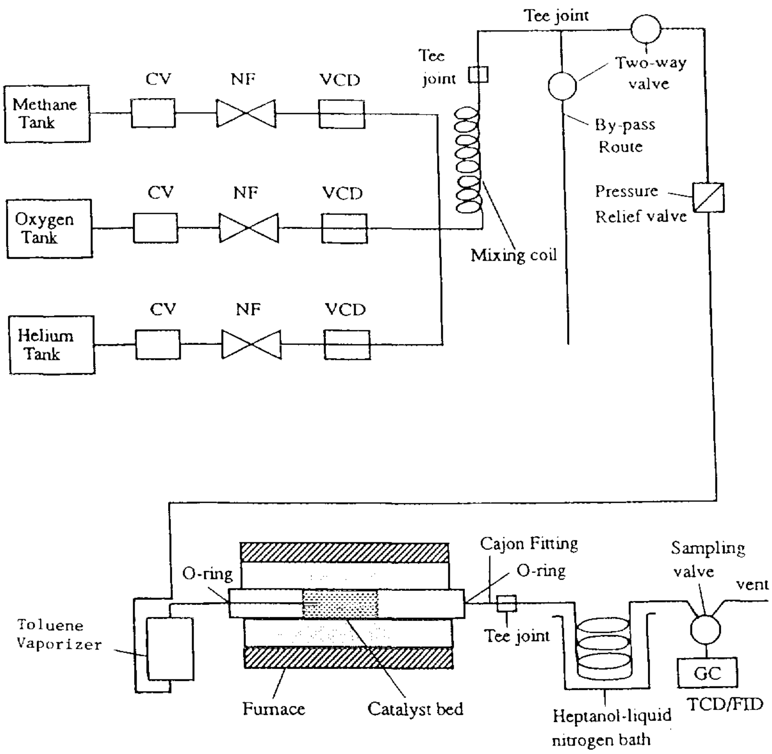


FIG. 1. Schematic diagram of the reactor setup used in the oxidative methylation of toluene. CV—check valve; NF—Nupro filter; VCD—variable constant differential flow controller.

pressed as the fraction of moles of toluene reacted. The selectivity is the ratio of the number of moles of a particular product to the total number of moles of all the products (without water). The yield is the product of the conversion and the selectivity.

Catalyst Characterization

The catalysts were characterized by surface area measurements (BET method), X-ray diffraction (XRD) analysis, atomic absorption spectrophotometry (AAS), X-ray photoelectron spectroscopy (XPS), and basicity/base strength distribution measurements. The details of the methods have been reported previously (*23, 26*). The basicity and the base strength distribution of the solid catalysts were determined by two methods: benzoic acid titration using indicators (*22, 27*), and gaseous acid (CO_2) adsorption followed by its stepwise thermal desorption (*28, 29*). The base strength of a solid surface is defined as the ability of the surface to donate an electron pair to an adsorbed acid. The amount of basicity (or basic sites) on a solid is expressed as the number (or mmol) of basic sites per unit weight or per unit surface area of the solid. The surface area of some calcined samples and the alkali metal loadings determined by AAS are presented in Table 1.

RESULTS

Noncatalytic Reactions

The oxidative methylation of toluene (i.e., the reaction involving methane, oxygen, and toluene vapor with helium as a diluent) was carried out in an empty (no catalyst) reactor both in the absence and the presence of quartz wool plugs at 650–850°C in order to examine the contribution of the

TABLE 1

Some Physicochemical Characteristics of the MgO-Supported Mono- or Bialkali Metal Sulfate(s)

No.	Sample[a]	Surface area (m^2/g)	Alkali metal loadings[b] (mol%) Before calcination	Alkali metal loadings[b] (mol%) After calcination
1.	MgO	14.5	—	—
2.	Li_2SO_4/MgO	8.8	10	3.4
3.	Na_2SO_4/MgO	9.5	10	9.5
4.	K_2SO_4/MgO	9.2	10	9.0
5.	Rb_2SO_4/MgO	10.0	10	2.5
6.	Cs_2SO_4/MgO	8.5	10	9.6
7.	(Li_2SO_4 + Na_2SO_4)/MgO	6.2	5 + 5	1 + 4.7
8.	(Li_2SO_4 + K_2SO_4)/MgO	5.8	5 + 5	0.6 + 4.4
9.	(Li_2SO_4 + Rb_2SO_4)/MgO	6.5	5 + 5	0.5 + 0.3
10.	(Li_2SO_4 + Cs_2SO_4)/MgO	7.0	5 + 5	0.8 + 4.6
11.	(Na_2SO_4 + K_2SO_4)/MgO	5.5	5 + 5	4.6 + 4.4
12.	(Na_2SO_4 + Rb_2SO_4)/MgO	5.2	5 + 5	4.8 + 1.0
13.	(Na_2SO_4 + Cs_2SO_4)/MgO	6.8	5 + 5	4.8 + 4.8
14.	(K_2SO_4 + Rb_2SO_4)/MgO	5.4	5 + 5	4.0 + 0.6
15.	(K_2SO_4 + Cs_2SO_4)/MgO	6.0	5 + 5	3.4 + 4.5
16.	(Rb_2SO_4 + Cs_2SO_4)/MgO	6.4	5 + 5	0.8 + 4.7

[a] Crystalline phases identified by XRD are MgO only, except for samples 3 and 6, which showed additional phases of Na_2SO_4 and Cs_2SO_4, respectively.

[b] AAS analysis showed that the initial alkali loadings are approximately the same after calcination, except for the Li- and Rb-containing samples, which showed a substantial loss of those elements during calcination.

non-catalytic (thermal gas-phase reactions) reactions to the catalytic one. The results obtained at 750°C are presented in Table 2. Below 700°C the empty reactor gave only CO and CO_2, but above 700°C, in addition, small amounts of benzene, ethylbenzene, styrene, stilbene, bibenzyl, and water were observed. A C_8-yield of 0.6 and 1.3% in the absence and presence of quartz wool plugs, respectively, indicates that some methylation of toluene took place thermally. However, this contribution is insignificant compared to the catalytic performances.

Catalytic Performances

Pure MgO (s–g) and mono- or bialkali-metal-compounds-promoted MgO are low-surface-area (<15 m^2/g) crystalline materials (Table 1). Upon promoting MgO with the alkali metal sulfate(s), the surface areas of the resulting materials decreased. These decreases are more noticeable with the bialkali-promoted MgO than with the mono-alkali-promoted ones. Similar results were obtained in our previous investigation (*23*) over mono- and bialkali-metal-hydroxide-promoted MgO.

In spite of the decreases in surface area, the catalytic performances of the bialkali (from the hydroxides, chlorides, sulfates, acetates, carbonates or nitrates precursors) promoted MgO were significantly higher than those of any monoalkali-promoted MgO or pure MgO (as shown later). The main products over all the catalysts were benzene, ethylbenzene, styrene, carbon oxides (both CO and CO_2), and H_2O with small amounts of xylene, stilbene, bibenzyl, and

TABLE 2

Oxidative Methylation of Toluene with Methane over Mono- or Bialkali-Metal-Sulfate(s)-Promoted MgO

Catalyst (alkali loading in mol%)	Conversion (mol%)			Selectivity (mol%)					Yield (%)	
	CH_4	O_2	C_7H_8	C_8H_{10} (EB)	C_8H_8 (ST)	Total C_8	C_6H_6 (BZ)	CO_x ($x = 1, 2$)	Total C_8	BZ
None	1.2	42	5.0	8.0	3.0	11.0	14.0	70	0.6	0.7
Quartz wool	1.7	54	7.4	11.4	6.0	17.4	12.5	65	1.3	0.9
10% Li^+/MgO	4.8	100	26.0	17.0	25.0	42.0	25.0	31.0	10.9	6.5
10% Na^+/MgO	5.0	100	27.0	17.0	26.0	43.0	22.0	30.0	11.6	5.9
10% K^+/MgO	3.8	98	24.0	15.0	20.0	35.0	25.0	35.0	8.4	5.5
10% Rb^+/MgO	3.5	97	22.0	15.5	21.8	37.3	26.0	34.0	8.2	7.5
10% Cs^+/MgO	4.8	100	25.5	16.0	26.5	42.5	23.0	30.0	10.8	7.6
(5%Li^+ + 5%Na^+)/MgO	10.3	100	42.0	24.0	32.0	56.0	19.0	20.0	23.5	8.0
(5%Li^+ + 5%K^+)/MgO	9.8	100	38.0	22.0	28.0	50.0	21.0	24.5	19.0	8.0
(5%Li^+ + 5%Rb^+)/MgO	9.0	100	38.0	22.0	25.0	47.0	23.0	25.0	17.9	8.7
(5%Li^+ + 5%Cs^+)/MgO	11.5	100	41.0	23.0	31.0	54.0	20.0	23.0	22.1	8.2
(5%Na^+ + 5%K^+)/MgO	11.0	100	40.5	21.0	31.0	52.0	21.0	24.0	21.1	8.5
(5%Na^+ + 5%Rb^+)/MgO	8.8	100	37.0	25.0	26.0	49.8	20.0	25.0	18.1	7.4
(5%Na^+ + 5%Cs^+)/MgO	12.0	100	42.5	22.0	35.0	57.0	18.0	21.0	24.2	7.5
(5%K^+ + 5%Rb^+)/MgO	8.2	98	36.0	21.0	24.0	45.0	23.0	28.0	16.2	8.3
(5%K^+ + 5%Cs^+)/MgO	10.5	100	41.0	26.0	25.0	51.0	21.0	23.0	20.9	8.6
(5%Rb^+ + 5%Cs^+)/MgO	9.2	100	39.5	22.5	27.2	49.7	21.0	24.0	19.6	8.3

Note. Reaction conditions: $T = 750°C$, $P = 1$ atm, total flow = 50 ml/min (NTP), $P_{CH_4} : P_{O_2} : P_{C_7H_8} : P_{He} = 14.7 : 2.9 : 1 : 11.8$, and space velocity = 15,000 $cm^3\ g^{-1}\ h^{-1}$. The results were obtained after 3 h of reaction.

C_2 hydrocarbons and a trace amount of unidentified hydrocarbons. No phenol or aldehyde was detected in the product. Pure MgO (s–g) showed some performance with a total C_8-selectivity (ethylbenzene + styrene) of 21.6 mol% and a C_8-yield of 3.4%; the benzene yield was 3.1% (Table 3). These values are higher than those in the noncatalytic reactions but much lower than those over the mono- or bialkali-promoted MgO. The oxygen conversion increased noticeably up to 98%. Carbon oxides were the dominant products.

Monoalkali-Metal-Compound-Promoted MgO

Upon promoting MgO (s–g) with any monoalkali metal compound (sulfate, hydroxide, chloride, acetate, carbonate, or nitrate), substantial increases in toluene conversion and C_8-selectivity were obtained, the methane conversion increasing to some extent compared to the results obtained over pure MgO. Since the performances of the catalysts obtained from the first three precursors (sulfate, hydroxide, or chloride) were much higher than those from the latter three, only those results are presented in Tables 2–4. The selectivity to benzene remained almost the same as for pure MgO, whereas that to carbon oxides showed some decrease (Tables 2–4). Among the alkali metals, Na^+/MgO showed the best performance in terms of C_8-yield, followed closely by Cs^+/MgO and Li^+/MgO. The other two monoalkali-promoted MgO, namely, K^+/MgO and Rb^+/MgO, were less effective under the same conditions. The oxygen conversions, however, were very high (>97 mol%) over all the promoted MgO as for pure MgO. Depending on the nature of the alkali cation and to a smaller extent on the nature of the associated anion, the promoted MgO exhibited varying performances, with the total C_8-selectivity between 29.5 and 43.0 mol%, and the total C_8-yield between

TABLE 3

Oxidative Methylation of Toluene with Methane over Mono- or Bialkali-Metal-Hydroxide(s)-Promoted MgO

Catalyst[a] (alkali loading in mol%)	Conversion (mol%)			Selectivity (mol%)					Yield (%)	
	CH_4	O_2	C_7H_8	C_8H_{10} (EB)	C_8H_8 (ST)	Total C_8	C_6H_6 (BZ)	CO_x (x = 1, 2)	Total C_8	BZ
MgO	2.6	98	15.7	14.0	7.6	21.6	20.0	48	3.4	3.1
10% Li^+/MgO	4.8	100	25.0	15.0	24.0	39.0	22.4	35	9.7	5.6
10% Na^+/MgO	4.0	100	22.6	18.0	20.5	38.5	22.0	36	8.7	6.3
10% K^+/MgO	3.2	100	24.4	15.0	19.0	34.0	24.2	42	8.3	5.9
10% Rb^+/MgO	3.0	98	23.0	19.2	13.0	32.2	21.2	23	7.4	6.2
10% Cs^+/MgO	5.1	100	25.2	14.0	24.8	38.8	23.0	34	9.8	6.2
(5%Li^+ + 5%Na^+)/MgO	9.7	100	41.2	24.0	30.2	54.2	21.2	23	22.3	8.7
(5%Li^+ + 5%K^+)/MgO	9.0	99	39.0	23.0	26.0	49.0	20.5	27	19.1	8.0
(5%Li^+ + 5%Rb^+)/MgO	8.7	100	37.4	25.0	22.4	47.4	22.3	27	17.7	8.3
(5%Li^+ + 5%Cs^+)/MgO	11.0	100	40.0	22.0	32.0	54.0	19.6	24	21.6	7.8
(5%Na^+ + 5%K^+)/MgO	10.4	98	40.3	20.0	32.4	52.4	19.8	26	21.1	8.0
(5%Na^+ + 5%Rb^+)/MgO	8.5	100	37.0	26.0	24.2	50.2	20.2	27	18.6	7.5
(5%Na^+ + 5%Cs^+)/MgO	11.8	100	40.7	22.0	34.0	56.0	18.5	23	22.8	7.5
(5%K^+ + 5%Rb^+)/MgO	8.0	97	35.0	23.0	21.0	44.0	23.0	29	15.4	8.0
(5%K^+ + 5%Cs^+)/MgO	10.3	100	40.2	27.0	24.2	51.2	20.0	28	20.6	8.0
(5%Rb^+ + 5%Cs^+)/MgO	8.7	100	39.0	22.3	27.0	49.3	21.6	26	19.2	8.4

Note. Reaction conditions are as in Table 2.

[a] The surface areas of the samples are between 5 and 15 m^2/g.

TABLE 4

Oxidative Methylation of Toluene with Methane over Mono- or Bialkali-Metal-Chloride(s)-Promoted MgO

Catalyst (alkali loading in mol%)	Conversion (mol%)			Selectivity (mol%)					Yield (%)	
	CH_4	O_2	C_7H_8	C_8H_{10} (EB)	C_8H_8 (ST)	Total C_8	C_6H_6 (BZ)	CO_x (x = 1, 2)	Total C_8	BZ
10% Li^+/MgO	3.3	100	22.0	13.0	29.0	32.0	25.0	40.0	7.0	5.5
10% Na^+/MgO	4.2	100	23.0	15.0	20.0	35.0	22.0	40.0	8.0	5.1
10% K^+/MgO	3.0	97	20.0	12.0	18.0	30.0	23.0	43.0	6.0	4.6
10% Rb^+/MgO	2.7	98	18.0	12.5	17.0	29.5	24.0	44.0	5.3	4.3
10% Cs^+/MgO	4.0	100	22.0	16.0	20.0	36.0	23.0	38.0	7.9	5.1
(5%Li^+ + 5%Na^+)/MgO	9.0	100	38.0	22.0	28.0	50.0	20.0	29.0	19.0	7.6
(5%Li^+ + 5%K^+)/MgO	8.0	100	33.0	20.0	25.5	45.5	22.0	30.5	15.0	7.3
(5%Li^+ + 5%Rb^+)/MgO	7.4	100	29.0	20.0	23.0	43.0	25.0	32.0	12.5	6.7
(5%Li^+ + 5%Cs^+)/MgO	9.8	100	37.0	21.0	29.0	50.0	23.0	25.0	18.5	8.5
(5%Na^+ + 5%K^+)/MgO	9.5	100	35.0	20.0	27.0	47.0	24.0	25.0	16.4	8.4
(5%Na^+ + 5%Rb^+)/MgO	7.6	97	31.0	18.8	23.0	41.8	21.0	31.0	12.9	6.5
(5%Na^+ + 5%Cs^+)/MgO	10.8	100	40.0	21.0	30.0	51.0	22.0	25.0	20.4	8.8
(5%K^+ + 5%Rb^+)/MgO	7.0	98	30.0	19.0	21.0	40.0	24.0	34.0	12.0	7.2
(5%K^+ + 5%Cs^+)/MgO	8.4	100	37.0	20.0	26.0	46.0	24.0	28.0	17.0	10.3
(5%Rb^+ + 5%Cs^+)/MgO	7.5	100	34.0	19.3	26.0	45.0	24.0	27.0	15.3	8.2

Note. Reaction conditions are as in Table 2.

5.3 and 11.6%. Thus, Na_2SO_4/MgO showed the highest toluene conversion of 27.0 mol% and total C_8-selectivity of 43%, with a styrene/ethylbenzene ratio of 1.5, whereas RbCl/MgO was found to be the least effective catalyst. In general, in terms of the total C_8-yields the following sequence for the alkali cations was observed: $Na^+ > Cs^+ > Li^+ > K^+ > Rb^+$. A similar sequence was also observed for the alkali cations associated with acetate, carbonate, or nitrate (these results are not included in the paper for the sake of brevity). However, their performances were somewhat lower than those observed for the sulfates, hydroxides, or chlorides precursors. In terms of the influence of the anions, the following sequence was observed: $SO_4^{2-} > OH^- > Cl^- > AC^- > CO_3^{2-} > NO_3^-$, the differences being quite small, however.

Bialkali-Metal-Compounds-Promoted MgO

Upon promoting MgO (s–g) with any of the bialkali metal compounds (total loading 10 mol% with equal molar contents), such as LiA + NaA, LiA + CsA, NaA + CsA, or KA + CsA (A = SO_4^{2-}, OH^-, Cl^-, CH_3COO^-, CO_3^{2-}, or NO_3^-), via simultaneous impregnation with both the compounds, significant increases in toluene and methane conversions and, particularly, in the total C_8-selectivity were observed, compared to those over the respective monoalkali-promoted MgO systems. The results obtained over 10 different MgO-supported bialkali derived from the first three precursors (SO_4^{2-}, OH^-, and Cl^-) are presented in Tables 2–4. The oxygen conversions (97–100 mol%) were as high as in the other cases. Both the selectivities to benzene and carbon oxides decreased to some extent. The styrene/ethylbenzene ratios did not vary much compared to those over the monoalkali-promoted MgO.

The catalytic performances, however, depend on the nature of the alkali compounds forming the pair, the anions associated with the cations and the reaction conditions. Thus, the maximum steady-state methane and toluene conversions (12.0 and 42.5 mol%, respectively) and the highest total C_8-selectivity of 57 mol% (ethylbenzene 22.0 and styrene 35.0 mol%) were obtained over (5 mol% Na^+ + 5 mol% Cs^+)/MgO (prepared from the sulfate precursors). This gives rise to a total C_8-yield of 24.2%, which is much higher than the monoalkali-promoted MgO. This is the highest C_8-yield ever reported in the open literature. Over this catalyst the benzene yield was only 7.5%, which is almost the same as that over the monoalkali-promoted MgO. Other bialkali promoted MgO (e.g., LiA + CsA, LiA + NaA, or KA + CsA, where A = SO_4^{2-}, OH^-, Cl^-, CH_3COO^-, CO_3^{2-}, or NO_3^-) also showed noticeable increases in the total C_8-yield, the benzene yield remaining nearly the same as for monoalkali-promoted MgO. The least effective among the bialkali systems was (5 mol% KNO_3 + 5 mol% $RbNO_3$)/MgO with a toluene conversion of 24.0 mol% and a total C_8-selectivity of 35.0 mol%, i.e., a total C_8-yield of only 8.4% (not shown in the table). Even then these values are much higher than those obtained over any monoalkali-promoted MgO. In general, Na^+ and Cs^+ pair was the most effective, whereas the K^+ and Rb^+ pair was the least in enhancing the catalytic performances. In terms of the influence of the anions a similar sequence as that for the monoalkali-promoted systems was observed, i.e., SO_4^{2-} was the most and NO_3^- the least effective. However, the effects of the bialkali cations were much more pronounced than the influence of the anions.

Effect of Alkali Loadings

Since the promoter effects of the pairs originating from the combination of Li_2SO_4, Na_2SO_4, or Cs_2SO_4 on MgO were the most pronounced, further investigations regarding the effects of the alkali loadings, reaction temperature, stability with time-on-stream, space velocity, and partial pressures of the reactants concentrated on such systems. Figures 2a and 2b present the effects of the

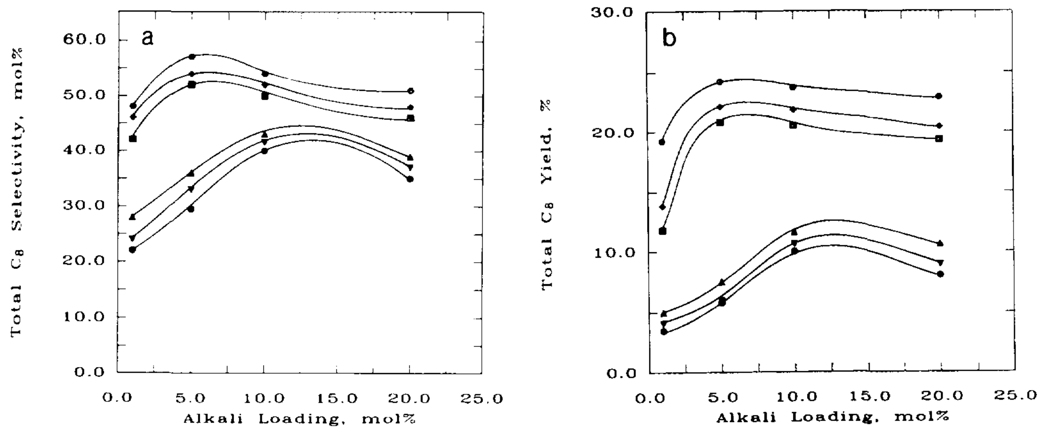


FIG. 2. Effects of the alkali loadings on the total C_8-selectivity (a) and the total C_8-yield (b) over mono- or bialkali-metal-sulfate(s)-promoted magnesia. Reaction conditions: Temperature = 750°C, pressure = 1 atm, $CH_4 : O_2 : C_7H_8 : He = 14.7 : 2.9 : 1 : 11.8$, and space velocity = 15,000 $cm^3g^{-1}h^{-1}$. The products are measured after 3 h of reaction. ●, Li^+/MgO; ▼, Na^+/MgO; ▲, Cs^+/MgO; ■, $(Li^+ + Na^+)/MgO$; ◆, $(Li^+ + Cs^+)/MgO$; ⬢, $(Na^+ + Cs^+)/MgO$. For bialkali the loadings of the two are equal; only the loading of one of the alkali is marked on the abcissa.

mono- or bialkali metal sulfate loadings on the performances (total C_8-selectivity and yield) of the resulting catalysts. The alkali loadings were varied from 1 to 20 mol% for the monoalkali-promoted systems, whereas the total alkali loadings for the bialkali-promoted systems from 2 to 40 mol% with an equal molar amount of both the alkalis. With the increase in alkali loadings, the monoalkali-promoted systems derived from the sulfate precursors show enhanced C_8-selectivity and C_8-yield, the 10 mol% systems exhibiting the highest performances (Fig. 2). Of these systems, 10% Na^+/MgO was the best with a total C_8-selectivity of 43.0 mol% and a total C_8-yield of 11.6%. The methane and toluene conversions also increased, remaining, however, almost constant for loadings higher than 10 mol% M^+/MgO. The benzene selectivity does not change much with the alkali loading, but its yield increases due to the increase in the toluene conversion. The selectivity to carbon oxides continued to increase and became 38 mol% over 20% K^+/MgO (not shown in the figure). However, the effect of the alkali loading on the monoalkali-promoted systems was much lower than those obtained with any bialkali-promoted systems. For the latter, the best performances were observed over (5 mol% Na^+ + 5 mol% Cs^+)/MgO, exhibiting the highest C_8-selectivity (57.0 mol%) and C_8-yield (24.2%). For the other two bialkali systems, the highest performances were also exhibited by the (5 mol% Li^+ + 5 mol% Cs^+)/MgO and (5 mol% Li^+ + 5 mol% Na^+)/MgO systems. The systems with [10 mol% Na^+ (Li^+ or Cs^+) + 10 mol% Cs^+ (Na^+ or Li^+)] also showed good performances but slightly lower than the former systems. Further increases in the alkali loadings (higher than 10 mol% for each) decreased the C_8-selectivity and the C_8-yield.

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

Figures 3a and 3b present the reaction temperature dependence of the total C_8-selectivity and the total C_8-yield over some of the mono- or bialkali-metal-sulfate-promoted MgO. For the monoalkali promoted systems, the toluene conversion increases as the reaction temperature increases from 650 to 850°C, but the total C_8-selectivity passes through a maximum (42–43 mol%) at 750°C, the 10% Na^+/MgO exhibiting the

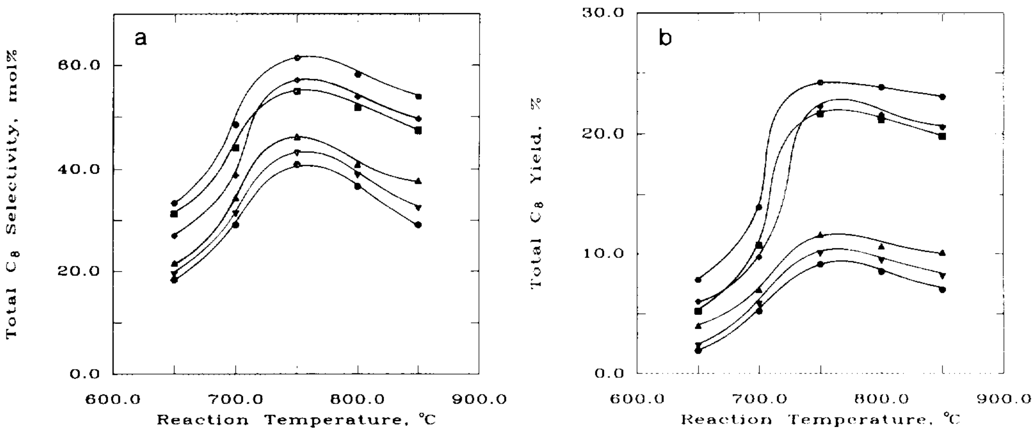


FIG. 3. Effects of reaction temperatures on the total C_8-selectivity (a) and the total C_8-yield (b) over mono- or bialkali-metal-sulfate(s)-promoted magnesia. The symbols and the reaction conditions are as in Fig. 2, except the temperature. For monoalkali the loading is 10 mol% and for bialkali the loading of each alkali is 5 mol%.

highest C_8-selectivity (Fig. 3a). For the bialkali-promoted systems a similar trend is observed, but with much higher toluene conversion, which increases up to 43–46 mol% at 850°C, and significantly higher C_8-selectivity, which also passes through a maximum (54–57 mol%) at 750°C, than the respective monoalkali systems. A similar effect of the reaction temperature on the C_8-selectivity and the C_8-yield was observed over NaBr/La_2O_3 catalysts (*16*). The (5 mol% Na^+ + 5 mol% Cs^+)/MgO exhibited the highest performances at all temperatures. At temperatures higher than 750°C, the carbon oxides predominate in the products over all catalysts.

A prominent difference between the mono- and the bialkali-metal-compound-promoted MgO was observed with time-on-stream. The stability with time-on-stream of the bialkali-promoted systems is much higher than that of the monoalkali promoted systems (Figs. 4a and 4b). Thus, during 60 h of operation the total C_8-selectivity over the monoalkali-promoted systems suffered a 50–55% decrease compared to the initial value, the 10 mol% Li^+/MgO being the least stable one (Fig. 4a). In contrast, the C_8-selectivity over the bialkali-metal-sulfate-promoted MgO remained almost unchanged. Toluene conversions also suffered noticeable decreases (25–30 mol%) over the former systems, unlike over the latter ones, which showed a negligible decrease. This gave rise to much higher and stable with time-on-stream C_8-yields over the bialkali-promoted systems than over the monoalkali-promoted systems (Fig. 4b). Again, the (5 mol% Na^+ + 5 mol% Cs^+)/MgO was the most stable. During this prolonged operation, coke deposition was observed on all the catalysts, particularly on the bialkali-promoted systems. In spite of this coke deposition, the selectivity to styrene continuously increased (at least for 3 h), while that to ethylbenzene decreased. A similar observation was made as early as 1972 for different catalytic systems (*30*).

Effects of the Pseudo-contact Time

In order to determine the effects of the pseudo-contact time (or the reciprocal space velocity *W*/*F*), the amount of catalyst (*W*) was varied while holding the flow rate (*F*) constant. Figures 5a and 5b present the effect of the pseudocontact time on the total C_8-selectivity and C_8-yield over some mono- or bialkali-metal-sulfate-promoted MgO.

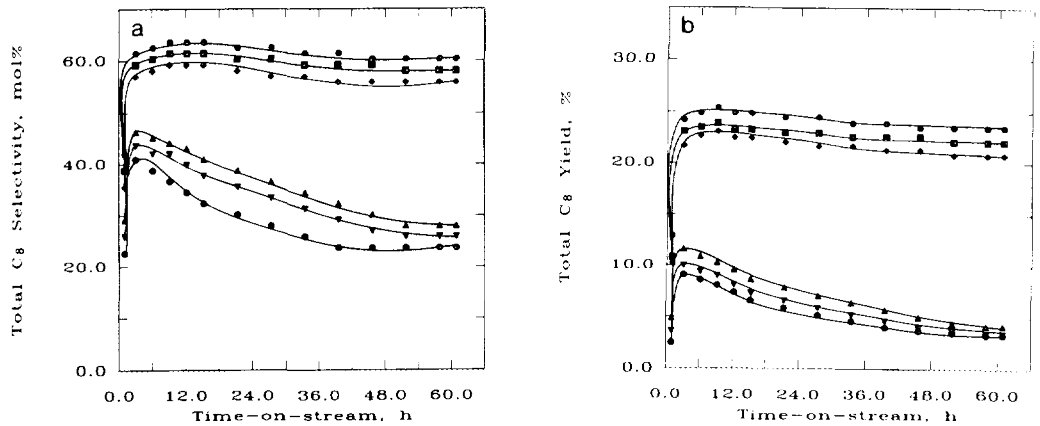


FIG. 4. Change in the total C_8-selectivity (a) and the total C_8-yield (b) with time-on-stream over the mono- or bialkali-metal-sulfate(s)-promoted magnesia. The symbols and the reaction conditions are as in Fig. 3, except the time-on-stream and the temperature which is 750°C.

For the monoalkali-promoted systems, the toluene conversion increases with *W/F*, the increase being more noticeable up to *W/F* = 0.24 g · s/ml. The total C_8-selectivity, however, passes through a maximum (42–43 mol%) at *W/F* = 0.24 g · s/ml, thereafter decreasing to some extent (Fig. 5a). There is little difference among the three monoalkali-promoted systems. The total C_8-yield also passes through a maximum (10.8–11.6%) at *W/F* = 0.24 g · s/ml, the 10 mol% Na^+/MgO showing the highest C_8-yield (Fig. 5b). For the bialkali-promoted systems, a similar pattern for the dependence on the pseudocontact time was observed, except that the C_8-selectivity and the C_8-yield are at higher levels than for the monoalkali-promoted systems. Also, the decreases with increasing pseudocontact time in C_8-selectivity and -yield are less than those in the monoalkali-

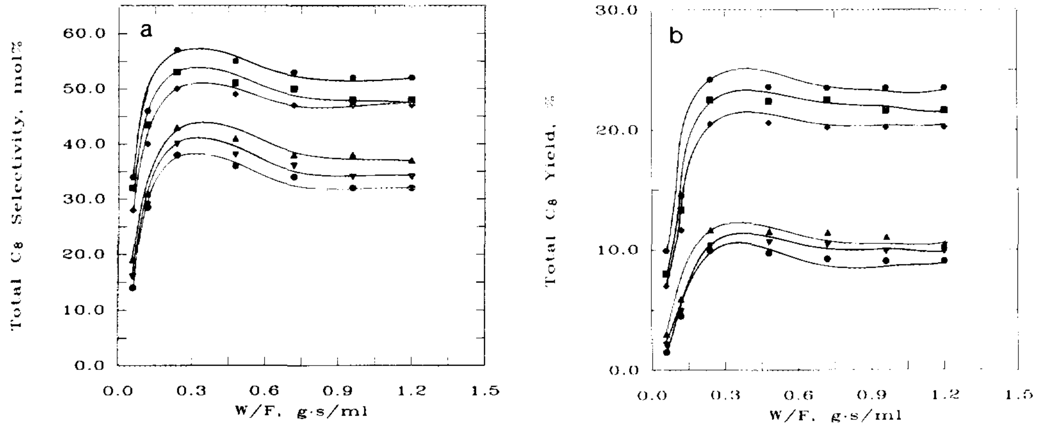


FIG. 5. Effects of pseudocontact time (*W/F*) on the total C_8-selectivity (a) and the total C_8-yield (b) over mono- or bialkali-metal-sulfate(s)-promoted magnesia. The symbols and the reaction conditions are as in Fig. 3, except the space velocity and the temperature which is 750°C.

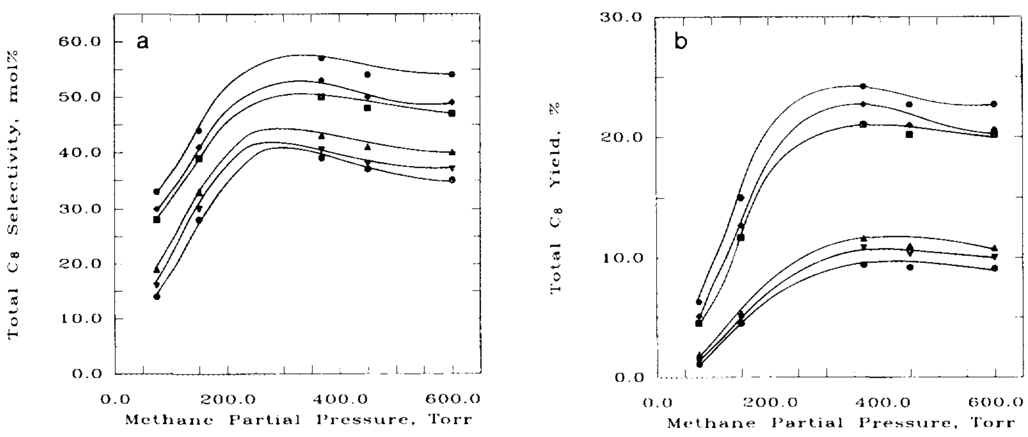


FIG. 6. Effects of methane partial pressure in the feed gas on the total C_8-selectivity (a) and the total C_8-yield (b) over mono- or bialkali-metal-sulfate(s)-promoted magnesia. The symbols and the reaction conditions are as in Fig. 3, except the methane partial pressure and the temperature which is 750°C.

promoted systems. These findings are approximately consistent with those in Ref. (*16*) obtained over different catalytic systems.

Effects of Reactant Partial Pressures

The effect of methane partial pressure on the C_8-selectivity and the C_8-yield over some of the mono- or bialkali-metal-sulfate-promoted MgO while holding the partial pressure ratios of the other components constant is presented in Figs. 6a and 6b. For the monoalkali-promoted systems, with increasing methane partial pressure the total C_8-selectivity increases, passing through a maximum (42–43 mol%) at $P_{CH_4} = 368$ Torr followed by some decrease (Fig. 6a). The C_8-yield also increases until $P_{CH_4} = 368$ Torr, thereafter showing a very small decrease due to the slight increase in toluene conversion (Fig. 6b). The bialkali-promoted systems show a similar pattern, but with much higher values for C_8-selectivity and C_8-yield. The highest C_8-selectivity (57.0 mol%) and C_8-yield (24.2%) were observed over (5 mol% Na^+ + 5 mol% Cs^+)/MgO.

Figures 7a and 7b show the effect of the partial pressure of toluene on the C_8-selectivity and the C_8-yield while keeping the partial pressure ratios of the other components constant. With the increase in partial pressure of toluene, the total C_8-selectivity increases over both the mono- and bialkali-promoted MgO and passes through a maximum at $P_{C_7H_8} = 25$ Torr (Fig. 7a). However, the bialkali-promoted systems have C_8-selectivities at much higher levels than the monoalkali-promoted systems. The C_8-yields over both the systems also exhibit similar patterns, with a relatively low decrease after $P_{C_7H_8} = 25$ Torr due to constant toluene conversion (Fig. 7b).

The effect of the partial pressure of oxygen on the total C_8-selectivity and the total C_8-yield is presented in Figs. 8a and 8b. The highest C_8-selectivity and C_8-yield over both the mono- and bialkali-promoted MgO were obtained at $P_{O_2} = 72.5$ Torr. Further increases in the oxygen partial pressure decreases the C_8-selectivity due to an increase in the formation of carbon oxides from toluene, whereas the C_8-yield leveled off at 8–9% and 21–22% for the monoalkali- and the bialkali-promoted systems, respectively.

Basicity and Base Strength Distribution

The basicity and base strength distribution of some mono- and bialkali-metal-sulfate-promoted MgO have been determined

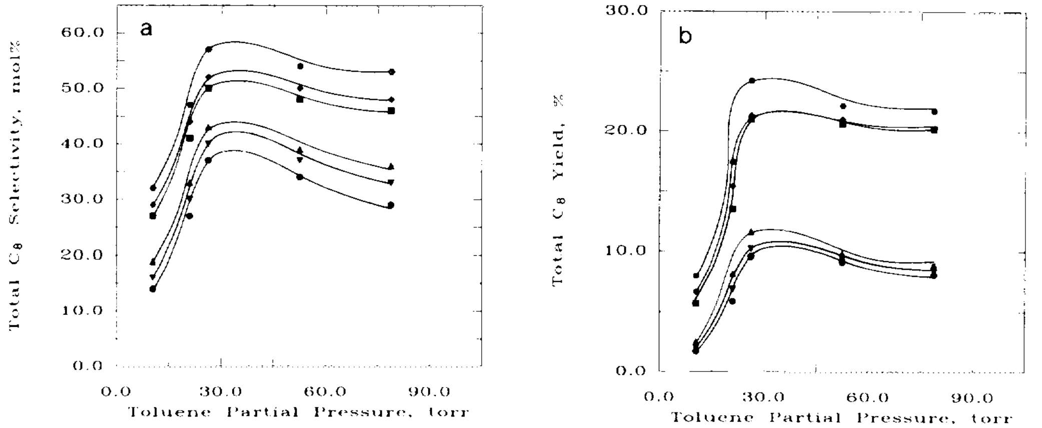


FIG. 7. Effects of toluene partial pressure in the feed gas on the total C_8-selectivity (a) and the total C_8-yield (b) over mono- or bialkali-metal-sulfate(s)-promoted magnesia. The symbols and the reaction conditions are as in Fig. 3, except the toluene partial pressure and the temperature which is 750°C.

by CO_2 adsorption followed by its stepwise thermal desorption (STD), and also by titration with benzoic acid in the presence of indicators. In the STD method, the amount of CO_2 chemisorbed on the catalyst at 50°C was determined 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 (*28*, *29*).

Figure 9 presents the basicity and base strength of pure MgO and of the mono- or bialkali-metal-sulfate-promoted MgO calcined *in situ* at 850°C for 15 h in a helium flow. Each column 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

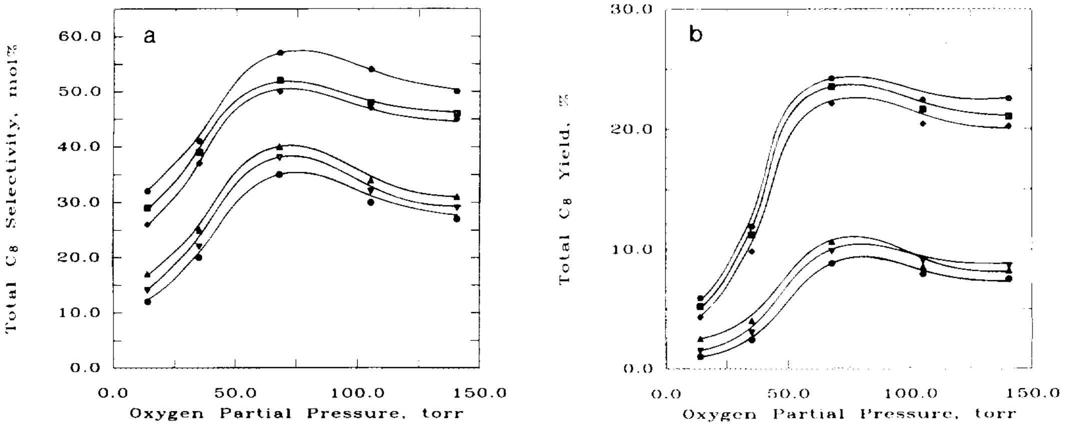


FIG. 8. Effects of oxygen partial pressure in the feed gas on the total C_8-selectivity (a) and the total C_8-yield (b) over mono- or bialkali-metal-sulfate(s)-promoted magnesia. The symbols and the reaction conditions are as in Fig. 3, except the oxygen partial pressure and the temperature which is 750°C.

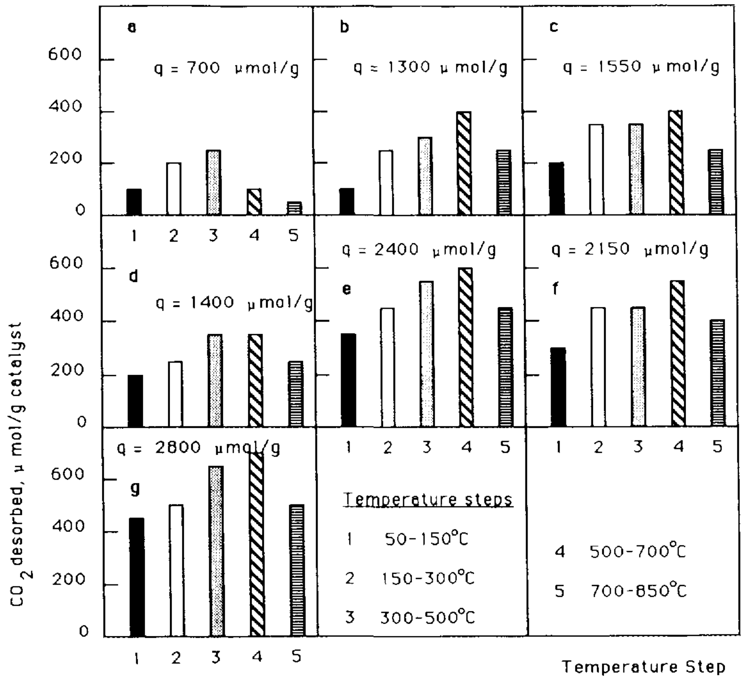


FIG. 9. Stepwise thermal desorption of preadsorbed CO_2 from the unpromoted and mono- or bialkali-metal-sulfate-promoted magnesia at 50–850°C (q = amount of CO_2 in μmol/g catalyst desorbed between 50–850°C). (a) MgO, (b) 10 mol% Li^+/MgO, (c) 10 mol% Na^+/MgO, (d) 10 mol% Cs^+/MgO, (e) (5 mol% Li^+ + 5 mol% Na^+)/MgO, (f) (5 mol% Li^+ + 5 mol% Cs^+)/MgO, (g) (5 mol% Na^+ + 5 mol% Cs^+)/MgO.

desorption temperatures of CO_2. As can be seen, upon promoting MgO (s–g) with mono- or bialkali metal sulfates, the amounts of desorbed CO_2 significantly increase, particularly for the latter systems, compared to pure MgO (s–g) (Fig. 9a). Moreover, the maximum desorption is shifted to higher temperatures than for pure MgO. A similar observation was made over mono- or bialkali-metal-chloride-promoted MgO previously (*23*).

Among the monoalkali promoted systems (Figs. 9b–9d), the 10 mol% Na^+/MgO showed the largest amount of CO_2 desorbed (1550 μmol/g cat) over the entire temperature range, and 250 μmol/g over the temperature range 700–850°C, which is close to the reaction temperature. For the bialkali-promoted systems (Figs. 9e–9g), the amounts of CO_2 desorbed are twice those for the respective monoalkali promoted systems. The largest CO_2 (2800 μmol/g) is desorbed from (5 mol% Na^+ + 5 mol% Cs^+)/MgO, indicating that this system possesses the highest basicity. Moreover, the basicity is quite high in the range 700–850°C, which can be seen from the large amount of CO_2 desorbed (500 μmol/g) in this range, close to the reaction temperature. The STD method was also used to measure the basicity and base strength distribution of some mono- and bialkali-promoted MgO catalysts subjected to the catalytic reaction for 60 h. A small increase of 10 to 20% was observed in the basicity and base strength distribution in these postcatalysis samples. This increase is, however, in the limit of experimental error.

A noticeable improvement in the basicity and base strength distribution of bialkali-

TABLE 5

Concentrations of Basic Ionic Sites on the Surface of MgO (s–g) and Mono- or Bialkali-Metal-Sulfate(s)-Promoted MgO (s–g) Calcined at 750°C, 15 h, as Measured by the Benzoic Acid Titration Method[a]

Sample (alkali loading in mol%)	Concentration of basic ionic sites (mmol/g)					
	$12.2 \leq H_-^b \leq 15.0$	$15.0 \leq H_- \leq 17.2$	$17.2 \leq H_- \leq 18.4$	$18.4 \leq H_- \leq 26.5$	$26.5 \leq H_- \leq 35.0$	Σ Sites (mmol/g)
MgO (s–g)	0.10	0.07	0.06	0.08	0.00	0.31
10%Li_2SO_4/MgO	0.17	0.11	0.11	0.14	<0.01	0.53
10%Na_2SO_4/MgO	0.18	0.14	0.13	0.12	<0.01	0.57
10%K_2SO_4/MgO	0.15	0.11	0.12	0.11	<0.01	0.49
10%Cs_2SO_4/MgO	0.18	0.11	0.12	0.15	<0.01	0.56
(5%Li_2SO_4 + 5%Na_2SO_4)/MgO	0.23	0.13	0.14	0.13	0.13	0.76
(5%Li_2SO_4 + 5%Cs_2SO_4)/MgO	0.23	0.13	0.15	0.14	0.14	0.79
(5%Na_2SO_4 + 5%K_2SO_4)/MgO	0.21	0.13	0.15	0.15	0.14	0.78
(5%Na_2SO_4 + 5%Cs_2SO_4)/MgO	0.22	0.14	0.15	0.15	0.16	0.82

[a] The accuracy is ±5%.

[b] H_- is the base strength determined from the pK_a value of an adsorbed indicator according to $H_- = pK_a + \log[B^-]/[BH]$, where pK_a is the negative logarithm of the dissociation constant of the indicator, [BH] is the concentration of the acidic form of the indicator, and $[B^-]$ is the concentration of the basic form; the $[B^-]/[BH]$ ratio is considered to be 1.

metal-sulfate-promoted MgO systems compared to the monoalkali-sulfate promoted MgO or pure MgO was also observed by the conventional method of titration with benzoic acid using indicators. However, this method is more qualitative than the STD method and the 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 the highly basic solids due to the presence of traces of moisture makes the determination of the end-point of titration difficult (*28*). Nevertheless, the results obtained still indicate that the basicity and base strength of the bialkali-promoted systems are higher than those of the monoalkali-promoted MgO.

It can be seen (Table 5) that only the bialkali-promoted MgO systems have an appreciable basicity in the range $26.5 \leq H_- \leq 35.0$ (fifth range), in addition to the noticeable basicity observed in the previous four successive ranges. In contrast, pure MgO and the monoalkali-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.* (*22*).

XPS Results

Some of the mono- or bialkali-metal-sulfate-promoted MgO were analyzed by XPS in order to get information on the valence states and the surface concentration of the elements. The electron-binding energies of the Li 1*s* (55.0 eV), Na 1*s* (1072.1 eV), Cs $3d_{5/2}$ (724.8 eV), Mg 2*s* (88.4 eV), O 1*s* (529.4 and 532.4 eV), and C 1*s* (285.0 and 289.7 eV) levels in both the mono- or bialkali-promoted MgO are in agreement (not shown here) with the reported values (*26, 31*). The binding energies indicate that the alkali metal elements are in the monovalent and magnesium in the divalent states, as expected. The O 1*s* and C 1*s* spectra, which have two different binding energies in the postcatalysis samples, provide evidence that multiple oxygen and carbon species are present on the surface of the catalysts. The higher binding energy of O 1*s* is ascribed to a carbonate-type, whereas the lower value to an oxide-type oxgyen (*26, 32*). For C 1*s* the lower binding energy is ascribed to graphite or hydrocarbons and the higher to carbonates (*26, 32*).

As we reported previously (*23*), some noticeable differences were observed between the surface compositions of the mono- and bialkali-promoted MgO systems derived from the chloride precursors, particularly after the catalytic reaction. The present study shows that in the monoalkali-promoted systems derived from the sulfate precursor, most of the Li in the surface layer was lost during calcination, unlike the surface Na or Cs which remained almost equal to the loading values (Table 6). A similar loss of surface Li was observed in other catalytic systems (*26, 29*). In contrast, the loss of surface Li in the calcined bialkali-promoted systems was less pronounced, and its surface concentration was equal to or slightly smaller than the loading value. On the other hand, the surface concentration of Na or Cs in these systems was higher than those corresponding to their loading values, and the total surface concentration of Na plus Cs was twice as high than that in the respective monoalkali-promoted systems for the same total molar loading. More importantly, after the catalytic reaction the surface concentration of Na and Cs, particularly of Na, significantly increased, in contrast to Li, which completely disappeared from the catalyst surface as in the Li-promoted MgO (Table 6).

DISCUSSION

Catalytic Performance

The present results demonstrate that upon promoting MgO (prepared via the sol–gel process or obtained commercially) with bialkali metal compounds, more active, selective and stable with time-on-stream catalysts than any monoalkali-compound-promoted MgO or pure MgO are obtained in the oxidative methylation of toluene with methane. Depending upon the nature of the promoter compounds forming the pair, the concentrations of the alkali ions and the reaction conditions, a noticeable improvement in the total C_8-yield (ethylbenzene and styrene) is obtained, which remains almost unchanged for a period of 60 h. The most effective catalytic systems are obtained with the bialkali metal compounds of LiA + NaA, LiA + CsA, KA + CsA, or NaA + CsA (A = SO_4^{2-}, OH^-, Cl^-, CH_3COO^-, CO_3^{2-}, or NO_3^-) containing an appropriate alkali loading (total 10 mol%) at 750°C (Tables 2–4). The nature of the cations forming the pairs exerts more influence on the catalyst performance than the anions associated with the cations. The four abovementioned pairs originating even from the least active anionic precursors (nitrates) show quite appreciable C_8-yields (15–16%). A similar effect was observed in the oxidative coupling of methane to C_2-hydrocarbons (*23*). It is apparent that while the anions play a part, their role is secondary. In fact, after calcination, the MgO-supported alkali compounds are converted into the corresponding alkali oxides, as evidenced by the absence of even traces of chlorine, sulfur, or nitrogen in the samples investigated by XPS. Thus, the nature of the alkali compounds forming the pair, the surface concentration of the alkali ions, and the reaction conditions are the key factors in determining the catalytic behavior of bialkali-promoted MgO.

The promoter effect of LiA + NaA, LiA + CsA, KA + CsA, or NaA + CsA (A = SO_4^{2-}, OH^-, Cl^-, CH_3COO^-, CO_3^{2-}, or NO_3^-) is synergistic, since individually none of these alkali-promoted MgO exhibits such high performances and the unsupported bialkali metal compounds were unsuitable for the high-temperature reaction. The difference in performance is clearly not a result of the surface area, because it was the lowest (5–7 m^2/g) for the bialkali-promoted 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 catalysts were less

TABLE 6

Surface Composition of the Elements in the Mono- and Bialkali-Metal-Sulfate(s)-Promoted MgO Determined by XPS[a]

Sample (alkali loading in mol%)	Surface atomic ratio[b]					
	Before reaction			After reaction		
	Li/Mg	Na/Mg	Cs/Mg	Li/Mg	Na/Mg	Cs/Mg
10% Li^+/MgO	0.01	—	—	0.00	—	—
10% Na^+/MgO	—	0.08	—	—	0.10	—
10% Cs^+/MgO	—	—	0.07	—	—	0.10
(5% Li^+ + 5%Na^+)/MgO	0.06	0.09	—	0.00	0.38	—
(5% Li^+ + 5%Cs^+)/MgO	0.05	—	0.08	0.00	—	0.28
(5% Na^+ + 5%Cs^+)/MgO	—	0.07	0.09	—	0.68	0.34

Note. All samples were calcined before reaction at 750°C, 15 h.

[a] For determining the binding energy of the elements, the value C 1*s* = 285.0 eV was used as a reference.

[b] Calculated from the atomic concentration determined by

$$C_x = \frac{I_x/S_x}{\Sigma_i I_i/S_i},$$

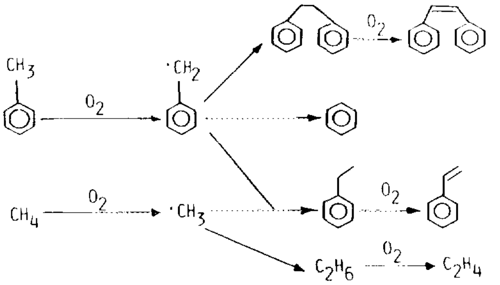
where I_x is the relative peak area of photoelectrons from element x and S_x is the atomic sensitivity factor.

effective. We observed a similar phenomenon while investigating these catalysts for the oxidative coupling of methane to C_2 hydrocarbons (*23*).

Effects of Alkali Loadings and the Operating Conditions

It was found that the best performances are exhibited by the bialkali promoted systems containing 5 or 10 mol% loading of each (Fig. 2). This indicates that such loadings are sufficient to generate active catalytic sites for the oxidative methylation of toluene. Further increases in the bialkali loadings decrease the performances, presumably because a too-large fraction of the MgO is covered. The striking differences between the mono- and bialkali-promoted MgO is not due to a loading effect, since the monoalkali-promoted MgO failed to show any comparable performance even at an alkali loading of 20 mol%.

The effects of the operating conditions (temperature, contact time, partial pressures of the reactants, etc.) on the performances of the mono- and bialkali-promoted MgO systems may allow us to propose possible routes for benzene, ethylbenzene, styrene, and carbon oxide formation (the main products observed in the present study). The reaction intermediates for the oxidative methylation of toluene with methane are hypothesized to be benzyl and methyl radicals, respectively (*7*). Based on this hypothesis, Otsuka *et al.* (*17*) have proposed the following mechanism:



Hence, in the presence of the catalyst and of a small amount of oxygen, benzyl and methyl radicals are formed by the abstraction of hydrogens followed by their cross-coupling to form a new C–C bond of ethylbenzene, which is partially dehydrogenated to styrene (C═C bond). Benzene is formed via the cleavage of C–C bond in the benzyl radical. A similar mechanism is likely to be valid in the present study also.

In the present study the effect of reaction temperature (Fig. 3) showed that even at a low temperature (650°C) a fairly high toluene conversion (~20 mol%) but a low C_8-yield (~4%) and some stilbene were obtained over the bialkali-promoted MgO. This is related to the possibility that even at such a low temperature the benzyl radical is formed but the methyl radical is not readily formed, and as a result the cross-coupling of the two radicals (benzyl and methyl) is less probable than the coupling of two benzyl radicals. The observation that with the increase in temperature the C_8-selectivity and C_8-yield pass through maxima at 750°C followed by a decrease indicates that at higher temperatures (>750°C) the cross-coupling of the radicals is less facilitated than their oxidation to carbon oxides and water. A similar observation was made by Suzuki *et al.* (*16*) over different catalysts.

The effect of the pseudocontact time on the product selectivity and yield may indicate the possible reaction path. The yields of benzene, ethylbenzene, carbon oxides, and C_{14} compounds increase proportionally at short contact time (low catalyst content) but at long contact times (high catalyst contents) all the yields decrease except that of carbon oxides (Fig. 4), which becomes the dominant product. It suggests that those products are formed in a parallel manner up to a certain contact time and at longer residence times in the catalyst bed the products are more prone to oxidation, particularly over the monoalkali-promoted systems than the bialkali-promoted MgO. This implies that, although the mechanism of product formations over both kinds of systems is apparently the same, the bialkali-promoted systems exhibit better performances than the monoalkali-promoted systems due to some intrinsic properties (such as basicity, as discussed below).

Substantial coke formation was observed on both the mono- or bialkali-promoted MgO, particularly during prolonged operations and on the latter systems. In spite of this coke deposition, the selectivity to styrene continuously increases, while that to ethylbenzene decreases. Such an observation may suggest that coke deposition on the catalyst may be beneficial for the formation of styrene from ethylbenzene. This is consistent with an earlier finding (*30*) that coke formation on alumina catalysts is the active catalytic material for oxydehydrogenation of ethylbenzene to styrene.

The partial pressure of methane in the feedstock was much larger than that of the other reactants and its increase (up to 368 Torr) enhances the C_8-selectivity and C_8-yield (Fig. 6), indicating that the increase of methyl radicals facilitates the combination with the benzyl radicals up to certain partial pressure of methane. The increase in the partial pressure of toluene (up to 25 Torr) is expected to enhance the formation of benzyl radicals, thus increasing the toluene conversion and C_8-selectivity and ultimately C_8-yield. While the toluene conversion continues to increase, the C_8-selectivity passes through a maximum, which may be due to some decrease in the combination between the benzyl and methyl radicals and an increase in the oxidation of toluene.

Unlike the methane and toluene conversions, the oxygen conversion was very high (>97 mol%) at any partial pressure over any catalyst, and this is in agreement with the findings of other groups (*16*, *18*). The lower conversion of methane than that of toluene may be related to the fact that the main part of the converted oxygen is used for toluene oxidation rather than activating the catalyst for methyl radical generation. With the increase in oxygen partial pressure (up to 72.5 Torr), the toluene conversion increases but the C_8-selectivity passes through a maximum at P_{O_2} = 72.5 Torr followed by a decrease. This happens because too much oxygen oxidizes the reaction intermediates and/or the C_8-products. Although the oxygen conversions are very high (>97 mol%) regardless of its partial pressure, we believe that the reaction conditions are outside the range of oxygen-limited conditions, because in the absence of any catalyst the oxygen conversion is much lower and the toluene conversion and the C_8-selectivity are very low.

Influence of the Basicity and Surface Concentration of Alkali

Although the striking differences observed between the mono- and 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 in the oxidative methylation of toluene. Indeed, high basicity was observed for some bialkali metal sulfates promoted MgO systems: (5 mol% Li^+ + 5 mol% Na^+)/MgO, (5 mol% Li^+ + 5 mol% Cs^+)/MgO, (5 mol% Na^+ + 5 mol% K^+)/MgO, and (5 mol% Na^+ + 5 mol% Cs^+)/MgO (Table 5 and Fig. 9). Because of their high basicity, these four catalysts can be considered as superbases, as already noted in the Results section. This is consistent with our previous findings of superbasicity with the bialkali-metal-chloride-promoted MgO used in the oxidative coupling of methane (*23*). The latter four catalysts exhibit significant performances in the oxidative methylation of toluene, but to a lesser extent than the sulfate or hydroxide precursors.

The mechanism of formation of superbasicity when MgO is promoted with certain bialkali metal compounds is less clear than its influence on the oxidative methylation of toluene or the oxidative coupling of methane. Although this phenomenon was first observed (*21*) some 15 years ago over Al_2O_3 or MgO, it is still far from clear. As suggested by Malinowskii *et al.* (*20*), the deposition of alkali metal ions onto MgO surface involves their interaction with the surface electron acceptor centers, such as the anion vacancies or the holes trapped on oxygen anions near the cation vacancies. The interaction between the alkali metal ions and the holes trapped on oxygen anions would give rise to electron pair donating sites, i.e., basicity of the surface. In the bialkali-metal-ion-promoted MgO, the number of basic sites is greater than in the monoalkali-promoted MgO because of the higher concentration of the alkali on the surface for the same molar loading. As a result, the amount of surface lattice oxygen (O^{2-}) having nucleophilic character (*33*) is also larger. Such lattice oxygen (O^{2-}) sites facilitate the abstraction of hydrogen from both methane and toluene.

The concentration of the alkali elements (Na and Cs) in the surface layer was much higher in the (Na^+ + Cs^+)/MgO (prepared from the chloride precursors) than in the respective monoalkali promoted MgO, particularly after 60 h of operation of oxidative coupling of methane. We suggested (*23*) that the high basicity is a result of the high enrichment of the surface layer with alkali ions. In the present study we observed a similar enrichment with the alkali (Na^+ and Cs^+) ions in the bialkali systems prepared from the sulfate precursors (Table 6). We are tempted to believe that the higher enrichment in the bialkali-promoted systems contributes to the noticeable performance for C_8-selectivity and stability with time-on-stream. Probably that new basic sites are generated which compensate for those lost due to aging (sintering, etc.). This may occur because the high concentrations of the promoting ions can generate new basic sites on the surface. The concentration of alkali ions in the surface layer for monoalkali-promoted systems is much lower, and this may explain why the activity and selectivity decrease in such cases with time. The somewhat lower performances and stability of the Li-containing bialkali systems could be attributed to the loss of the surface Li during the calcination and also during the reaction (as observed by XPS). It appears that the bialkali ions whose ionic radii are very different and which are less volatile, such as $Na^+ + Cs^+$, form the most effective catalytic systems. 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. This enrichment of the surface takes place because it decreases the surface free energy of the system. Our experiments have also shown that while the surface concentration of bialkali ions (determined by XPS) increases during the catalytic reaction, the basicity and the base strength distribution remain almost the same. This is probably due to the fact that XPS provides the concentration in a layer of about 10^2 Å, while the basicity measurements provide the concentration in a much thinner surface layer.

CONCLUSIONS

The following conclusions can be drawn from the present study on the effect of superbasic catalysts prepared by promoting MgO with the bialkali metal compounds on the oxidative methylation of toluene:

(1) A new class of highly basic (superbasic) catalysts, prepared by promoting MgO with various binary alkali metal compounds, such as LiA + NaA, LiA + CsA, KA + CsA, or NaA + CsA (A = SO_4^{2-}, OH^-, Cl^-, CH_3COO^-, CO_3^{2-}, or NO_3^-), is found to exhibit a synergistic effect in the selective formation of styrene and ethylbenzene via the oxidative methylation of toluene with methane. The most effective systems are obtained from SO_4^{2-}, OH^-, and Cl^- precursors. Any system containing a rubidium compound was less effective.

(2) The catalytic performances of the bialkali-metal-compounds-promoted MgO are significantly higher than those over any monoalkali-promoted MgO. Moreover, the stability with time-on-stream over the bialkali-promoted systems is much higher than over the monoalkali-promoted ones. The best catalytic performance is obtained over (5 mol% Na^+ + 5 mol% Cs^+)/MgO (prepared from the sulfate precursors), which exhibits a total C_8-yield of 24.2% (styrene/ethylbenzene = 1.6) compared to 11.6 and 10.8% over 5 mol% Na^+/MgO and 5 mol% Cs^+/MgO, respectively, at 750°C.

(3) The nature of the alkali compounds forming the pair, the concentration of the alkali promoters, and the reaction conditions are the key factors in determining the effectiveness of the systems. The influence of the alkali cations forming the pair is more pronounced than that of the anions associated with the alkali cations.

(4) The relatively high activity, selectivity, and stability with time-on-stream observed over the bialkali-promoted catalysts are attributed to the superbasicity of the resulting catalysts. The superbasicity of the bialkali-promoted systems is presumably due to the significant enrichment of the catalyst surface with the alkali ions, the presence of a second alkali enhancing the enrichment.

(5) A significant amount of Li^+ or Rb^+ is lost from the catalysts containing these elements during calcination and the catalytic reaction, unlike Na^+, K^+, or Cs^+. In spite of the loss, the Li^+-containing bialkali-promoted MgO showed high C_8-selectivity and stability with time-on-stream, unlike any Rb^+-containing sample.

REFERENCES

1. Lunsford, J. H., *in* "Natural Gas Conversion" (A. Holmen, K. J. Jens, and S. Kolboe, Eds.), Studies in Surface Science and Catalysis, Vol. 61, p. 3. Elsevier, Amsterdam, 1991.
2. Engvall, K., Holmlid, L., and Menon, P. G., *Appl. Catal.* **77,** 235 (1991).
3. Khcheyan, Kh. E., Revenko, O. M., Borisoglebskaya, A. V., and Fishman, D. L., *Zh. Org. Khim.* **12,** 467 (1976).
4. Khcheyan, Kh. E., Shatalova, A. N., Revenko, O. M., and Agrinskaya, L. I., *Neftekhimiya* **20,** 876 (1980).
5. Khcheyan, Kh. E., Revenko, O. M., Fradkov, Yu. Z., Borisoglebskaya, A. V., and Yakovich, N. I., USSR Patent 639845 (1978); *Chem. Abstr.* **90,** 559 (1979).
6. Khcheyan, Kh. E., Revenko, O. M., Borisoglebskaya, A. V., and Yakovich, N. I., *Neftekhimiya* **21,** 83 (1981).
7. Khcheyan, Kh. E., Revenko, O. M., and Shatalova, A. N., *in* "Proceedings of the 11th World Petroleum Congress, 1983," Vol. 4, p. 465.

8. Yakovich, N. I., Bokareva, L. P., and Kostyuk, A. G., "Pr-va Krupnotonnazh, Produktov Neftekhimii, Moskva, 1979," p. 37; *Chem. Abstr.* **93,** 775 (1980).

9. Lee, J. S., and Oyama, S. T., *Catal. Rev.-Sci. Eng.* **30,** 249 (1988).

10. Hutchings, G. L., Scurrell, M. S., and Woodhouse, J. R., *Chem. Soc. Rev.* **18,** 251 (1989).

11. Amenomiya, Y., Birss, V. I., Goledzinowski, M., Galuszka, J., and Sanger, A. R., *Catal. Rev.-Sci. Eng.* **32,** 163 (1990).

12. Osada, Y., Enomoto, K., Fukushima, T., Ogasawara, S., Shikada, T., and Ikariya, T., *J. Chem. Soc. Chem. Commun.*, 1156 (1989).

13. Suzuki, T., Wada, K., and Watanabe, Y., *Appl. Catal.* **53,** L19 (1989).

14. Osada, Y., Okino, N., Ogasawara, S., Fukushima, T., Shikada, T., and Ikariya, T., *Chem. Lett.*, 281 (1990).

15. Osada, Y., Ogasawara, S., Fukushima, T., Shikada, T., and Ikariya, T., *J. Chem. Soc. Chem. Commun.*, 1434 (1990).

16. Suzuki, T., Wada, K., and Watanabe, Y., *Ind. Eng. Chem. Res.* **30,** 1719 (1991).

17. Otsuka, K., Hatano, M., and Amaya, T., *J. Catal.* **137,** 487 (1992).

18. Kim, H., Suh, H. M., and Paik, H., *Appl. Catal.* **87,** 115 (1992).

19. Ruckenstein, E., and Khan, A. Z., *Catal. Lett.* **18,** 27 (1993).

20. Malinowskii, S., and Kijenskii, J., *in* "Catalysis" (C. Kemball and D. A. Dowden, Reporters), Vol. 4, p. 130. The Royal Society of Chemistry, London, 1980.

21. Kijenskii, J., and Malinowski, S., *J. Chem. Soc. Faraday Trans. I* **74,** 250 (1978).

22. Tanabe, K., Misono, M., Ono, Y., and Hattori, H., *in* "New Solid Acids and Bases" (B. Delmon and J. T. Yates, Eds.), Studies in Surface Science and Catalysis, Vol. 51, p. 14. Elsevier, Amsterdam, 1989.

23. Ruckenstein, E., and Khan, A. Z., *J. Catal.* **141,** 628 (1993).

24. Khan, A. Z., and Ruckenstein, E., *J. Chem. Soc. Chem. Commun.*, 587 (1993).

25. Lopez, T., Garcia-Cruz, I., and Gomez, R., *J. Catal.* **127,** 75 (1991).

26. Khan, A. Z., and Ruckenstein, E., *J. Catal.* **138,** 322 (1992).

27. Malinowskii, S., and Szczepanska, S., *J. Catal.* **2,** 310 (1963).

28. Choudhary, V. R., and Rane, V. H., *Catal. Lett.* **4,** 101 (1990).

29. Khan, A. Z., and Ruckenstein, E., *J. Catal.* **139,** 304 (1993).

30. Alkhazov, T. G., Lisovskii, A. E., Safarov, M. G., and Dadasheva, A. M., *Kinet. Katal.* **13,** 509 (1972).

31. Wagner, C. D., Riggs, W. M., Davis, L. E., Moulder, J. F., and Muilenberg, G. E. (Eds.), "Handbook of X-Ray Photoelectron Spectroscopy." Perkin–Elmer Corporation, Minnesota, 1978.

32. Miro, E., Santamaria, J., and Wolf, E. E., *J. Catal.* **124,** 451 (1990).

33. Baerns, M., and Ross, J. R. H., *in* "Perspectives in Catalysis" (J. M. Thomas and K. I. Zamaraev, Eds.), p. 315. Blackwell, London, 1992.