

Synergistic Effect of Bi-alkali-promoted MgO or CaO on Oxidative Methylation of Toluene with Methane: a Selective Route to Styrene and Ethylbenzene

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A new class of highly basic (superbasic) catalysts, prepared by promoting MgO or CaO with various binary alkali metal compounds such as NaA + CsA, LiA + CsA, LiA + NaA or KA + CsA (A = OH⁻, Cl⁻, AcO⁻, CO₃²⁻ or NO₃⁻) is found to exhibit a remarkable synergistic effect in the selective formation of styrene and ethylbenzene by oxidative methylation of toluene with methane.

Styrene, one of the most important industrial monomers, is produced by catalytic alkylation of benzene with ethylene over AlCl₃-HCl catalysts followed by oxidative dehydrogenation of the resulting ethylbenzene over potassium-promoted iron oxide catalysts. A different process for the production of ethylbenzene and, ultimately, styrene directly from toluene and methane, discovered by Khcheyan *et al.*,¹ provides an alternative route from abundant natural gas and distillates of coal tar, rather than from the limited petroleum sources, and minimizes pollution by hazardous catalysts such as AlCl₃-HCl. The latter authors reported that the oxides of Ni, Co, Mo, V along with alkali and alkaline earth metal oxides are effective catalysts, but details regarding the catalysts have not been disclosed. Recently, on the basis of catalysts² used for oxidative coupling of methane to C₂ hydrocarbons, several groups³ have employed some methane-coupling catalysts for the oxidative methylation of toluene with methane. However, such catalysts exhibit low selectivities towards the desired products and loss of alkali promoters during prolonged operation.

We recently observed⁴ that a substantial synergistic effect in the oxidative coupling of methane is obtained over bi-alkali-

promoted MgO compared with the effect produced by mono-alkali-promoted MgO. We attributed this effect to a significant enhancement of the basicity (superbasicity⁵) as a result of the deposition of bi-alkali metal compounds on MgO.

In this communication, we report on the synergistic effect of bi-alkali promoted MgO or CaO on the oxidative methylation of toluene with methane in the selective formation of ethylbenzene and styrene. We show that if MgO or CaO is promoted with two alkali metal compounds instead of one, superbasic catalysts are obtained which are more active, more selective for styrene and ethylbenzene and more stable with time-on-stream than the respective systems promoted with single alkali metal compounds.

MgO or CaO were either prepared by a sol-gel method involving the hydrolysis of the alkaline ethoxide dissolved in ethanol in the presence of an acid catalyst (HCl, pH = 3), or obtained commercially. No significant differences in the catalytic performance were observed between MgO (or CaO) prepared by the sol-gel method and that obtained commercially. The MgO or CaO powder thus obtained was calcined for 15 h at 900 °C, followed by impregnation with mono- or bi-alkali metal compounds, keeping the total alkali metal

Table 1 Catalytic performance for oxidative methylation of toluene with methane^a

Catalyst ^b (alkali loading in mol%)	Conversion (mol%)			Selectivity ^c (mol%)				Yield (%)		
	CH ₄	O ₂	C ₇ H ₈	C ₆ H ₅ CH ₂ CH ₃	C ₆ H ₅ CH=CH ₂	Total C ₈	C ₆ H ₆	CO _x (x = 1,2)	Total C ₈	C ₆ H ₆
Quartz wool	1.7	54	7.4	11.4	6.0	17.4	12.5	65	1.3	0.9
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	9.8	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	100	38.5	24.5	24.0	48.5	22.0	27	18.7	8.5
(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

^a Reaction conditions: $T = 750^\circ\text{C}$, $P = 1\text{ atm}$, total flow = 50 ml min^{-1} (NTP), $P(\text{CH}_4) : P(\text{O}_2) : P(\text{C}_7\text{H}_8) : P(\text{He}) = 14.7 : 2.9 : 1 : 11.8$ and space velocity = $15 \times 10^3\text{ cm}^3\text{ g}^{-1}\text{ h}^{-1}$. Results are after 3 h of reaction. ^b Alkali-promoted MgO catalysts were prepared from MOH precursors ($M = \text{Li, Na, K, Rb or Cs}$); the surface areas of the samples are $5\text{--}15\text{ m}^2\text{ g}^{-1}$. ^c The selectivity is calculated on the basis of moles of C_7H_8 converted.

content 10 mol%. 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. The catalytic runs were carried out under atmospheric pressure and at 750°C in a fixed bed flow reactor constructed from a high purity alumina tube (i.d. 6 mm) packed with 200 mg of catalyst and mounted horizontally inside a small programmable tube furnace. The reactant gas mixture of methane, oxygen and helium at a total flow rate of 50 ml min^{-1} (NTP) was passed through a toluene vapour saturator maintained at 22°C just before the inlet of the reactor, giving a pressure ratio, $P(\text{CH}_4) : P(\text{O}_2) : P(\text{C}_7\text{H}_8) : P(\text{He})$ of $14.7 : 2.9 : 1 : 11.8$. The gaseous and liquid products (trapped at -40°C) were analysed by a GC (Sigma 2000) fitted with Chromosorb and Bentone 34 columns (both $3.20\text{ mm} \times 1.82\text{ m}$) and a GC-MS (Hewlett-Packard 5890 Series II) fitted with a mass-selective detector (5971A) and three columns: a molecular sieve 5A ($3.20\text{ mm} \times 1.82\text{ m}$), a Poraplot wide-bore capillary ($0.53\text{ mm} \times 27.5\text{ m}$) and a cross-linked methyl silicone capillary ($0.20\text{ mm} \times 12.5\text{ m}$). The catalysts were characterized by surface area measurement, basicity and base strength distribution measurements and by X-ray photoelectron spectroscopy (XPS).

The main products were benzene, ethylbenzene, styrene and carbon oxides with small amounts of ethane, ethylene, water, xylene and trace amounts of stilbene and bibenzyl. Table 1 shows the results of the reaction at 750°C . The effect of the thermal reaction in the absence of the catalyst was also examined. A 1.3% yield of C_8 -products was observed, indicating that some methylation of toluene took place thermally. Both the methane and toluene conversions showed some increase over the five monoalkali-promoted MgO compared with unpromoted MgO. Among these monoalkali-promoted systems, the highest C_8 yield (9.8%) was obtained over 10 mol% Cs^+/MgO and the lowest (7.4%) over 10 mol% Rb^+/MgO . Compared to the unpromoted MgO, the toluene conversion increased up to 22.6–25.2 mol% and the benzene yield also increased to some extent, indicating that demethylation of toluene also occurs.

Upon promoting MgO with bi-alkali metal compounds (eq-molar quantities), significant increases in C_8 selectivity and toluene conversions were observed. A high C_8 yield of

22.8% (styrene 13.8% and ethylbenzene 9.0%) was obtained over (5 mol% $\text{Na}^+ + 5\text{ mol}\% \text{Cs}^+/\text{MgO}$). This is the highest C_8 yield ever reported in the open literature. (A total of 90% selectivity for benzene, ethylbenzene and styrene has been reported in the patent literature.¹) The benzene yield was only 7.5%, which is almost the same as in the monoalkali-promoted MgO. Other bi-alkali-promoted systems also showed noticeable increases in C_8 yield. The least effective among these systems was (5 mol% $\text{Li}^+ + 5\text{ mol}\% \text{Rb}^+/\text{MgO}$. Coke deposition was observed on all the catalysts, particularly on the bi-alkali-promoted ones. In spite of this coke deposition, the selectivity to styrene increased continuously for 3 h, while that to ethylbenzene decreased. This suggests that coke deposition on the catalyst may be beneficial for the formation of styrene from ethylbenzene. Such an observation was made as early as 1972.⁶

A prominent difference between the mono- and bi-alkali metal promoted MgO was observed with time-on-stream. During 60 h of operation, the former systems showed a 50% decrease in C_8 selectivity, whereas the latter ones remained almost unchanged. Toluene conversion also suffered a drastic decrease over the former systems, unlike over the latter ones.

The striking difference between mono- and bi-alkali promoted MgO systems is reflected in the basicity and base strength distribution measured by the benzoic acid titration method using indicators and by the gaseous CO_2 adsorption followed by its stepwise thermal desorption (STD). The benzoic acid titration method revealed that most of the bi-alkali-based systems have a base strength in the range $26.5 \leq H_- \leq 35.0$ ($H_- = \text{p}K$ of the indicator), which indicates that they are superbases, in accordance with the classification of Tanabe *et al.*⁷ The STD method showed that the largest amount of CO_2 ($2300\text{--}2750\text{ }\mu\text{mol g}^{-1}$) is also desorbed by the bi-alkali promoted systems, indicating that these systems possess the highest basicity and, more importantly, the basicity is quite high in the range of $700\text{--}850^\circ\text{C}$, which is close to the reaction temperature. The high basicity of the bi-alkali promoted MgO is probably due to the high enrichment of the surface with alkali atoms, as evidenced by XPS studies. The enrichment is much higher in the bi-alkali promoted systems than in the respective monoalkali-promoted systems. Apparently, the high catalytic performance of the bi-alkali-promoted

MgO is related to their high basicity and base strength distribution. Similar catalytic results were also observed for the bialkali-promoted CaO systems.

Experiments have been carried out also with alkali precursors other than hydroxides, namely Cl^- , AcO^- , CO_3^{2-} or NO_3^- . The best results have been obtained over hydroxides and are presented in Table 1. While the nature of the anion affects to some extent the performance, the major role is played by the bialkali cations.

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