Oxidative Methylation of Toluene with Methane over Alkali-promoted Y_2O_3–CaO Catalysts

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The Y_2O_3–CaO catalyst system, which is active for the oxidative coupling of methane to form C_2 hydrocarbons, catalysed the oxidative methylation of toluene using methane as the methylene source, to give ethylbenzene and styrene; the addition of alkali metal oxide greatly improved the selectivity in the order: $Li_2O > Na_2O > K_2O$.

The partial oxidation of methane is an attractive process for forming C_2 hydrocarbons. Recently a number of effective catalysts have been developed.[1—5] The reaction mechanism has been speculated to involve attraction of a hydrogen atom of methane to the active site of the catalyst to form a methyl radical and subsequent coupling of the methyl radicals.[1,6] This mechanism is applicable to the oxidative methylation of other hydrocarbons with methane to give higher hydrocarbons having a methyl or methylene group, and some attempts at this have been made. Sodesawa *et al.*[7] studied the formation of C_4 hydrocarbons by oxidative methylation of propene with methane over Na_2O/La_2O_3. Khcheyan *et al.*[8—11] reported the methylation of acetonitrile to give acrylonitrile, and that of toluene to give ethylbenzene and styrene. The latter reaction should provide a new route to synthesis of styrene monomer from natural gas and distillates of coal tar as an alternative to petroleum sources, and we investigated the application of catalysts which are effective for the oxidative coupling of methane to this reaction.

The carrier used here was Y_2O_3–CaO mixed oxide, an active and selective catalyst for the oxidative coupling of methane,[12] which was prepared by coprecipitation with oxalic acid. The coprecipitated oxalate was calcined in air at 800 °C for 3 h to form the mixed oxide. The ratio of Y_2O_3 to CaO was 1:9. The Y_2O_3–CaO catalysts were then doped with alkali metal oxides, Li_2O, Na_2O, and K_2O, by impregnation using the alkali metal nitrates or carbonates. Each catalyst was calcined in air at 700 °C for 3 h. The powdered catalyst was made into pellets, crushed, and then sieved (30—50 mesh) for charging into the quartz reactor. In order to compare the catalytic performance with the other active catalysts reported for the oxidative coupling reaction, PbO/MgO,[3] Li_2O/MgO,[1] Na_2O/La_2O_3,[7] and $K_2O/BaCO_3$[4] were also prepared by an impregnation method. In addition, Li_2O/SiO_2 catalyst was prepared for estimation of characteristics of the carrier. All the catalysts were calcined at 700 °C for 3 h. The reactions were carried out with 1.0 g of the catalyst in a conventional fixed-bed flow reactor (12 mm i.d.). The flow rates of feed gas were $CH_4/O_2/C_6H_5CH_3/H_2O/He = 25/4/2.5/19/5.5$ ml min^{-1}; toluene and water were fed as a liquid into a pre-heated zone, at about 300 °C, using a microfeeder. The highly volatile aromatic components in the gaseous product were trapped by a dry ice–methanol trap system, at about −70 °C. After reaction at 700 °C for 3.5 h, the trapped liquid components were recovered with acetone, and then aromatic hydrocarbons were analysed on PEG 20M and FFAP g.c. columns using a flame ionisation detector (f.i.d.), with *N,N*-dimethylformamide as an internal standard. The composition of effluents after the trap system was measured by an on-line thermal conductivity detector (t.c.d)–g.c. and f.i.d.–g.c. An active carbon column attached to a t.c.d. was used for analysis of H_2, O_2, CH_4, CO, and CO_2, while a Unibeads A column attached to an f.i.d. was used for analysis of C_2H_6, C_2H_4, C_3H_8, and C_3H_6.

Benzene, ethylbenzene, styrene, and trace amounts of stilbene, bibenzyl, propylbenzene, and xylene were detected on the analysis of the aromatic products. The selectivity and the yield of the main products, *i.e.*, benzene, ethylbenzene, and styrene, were calculated on the basis of toluene converted. Table 1 shows the results of the reaction on various catalysts. All the catalysts, which were effective for the oxidative coupling of methane, showed high activities to form the methylated products. However, carbonaceous deposits were observed on Y_2O_3–CaO and PbO–MgO after the

Table 1. Catalytic activity for oxidative methylation of toluene with methane.[a]

	Conversion/%			Selectivity/%[c]				Yield/%		
Catalyst[b]	CH_4	O_2	C_7H_8	C_8H_{10}	C_8H_8	Total C_8	C_6H_6	Total C_8	C_6H_6	Ratio of C_8/%[d]
20 wt% PbO/MgO	0.3	97.6	42.1	3.7	12.6	16.3	27.0	6.8	11.4	37.6
7 wt% Li_2O/MgO	4.3	85.5	27.1	25.0	12.2	37.2	10.7	10.1	3.0	77.7
3 wt% Na_2O/La_2O_3	3.9	96.8	28.5	17.4	7.6	25.0	11.7	7.2	3.4	68.1
3 wt% $K_2O/BaCO_3$	3.5	60.5	20.4	16.3	11.0	27.3	23.8	5.6	4.9	53.4
3 wt% Li_2O/SiO_2	3.2	100	21.8	4.9	0	4.9	11.6	1.1	2.5	29.7
Y_2O_3–CaO	3.9	100	34.8	10.7	8.2	18.9	23.5	6.6	8.2	44.6
3 wt% Li_2O/Y_2O_3–CaO	3.0	73.2	28.7	23.7	12.3	36.0	11.1	10.2	3.2	76.4
3 wt% Na_2O/Y_2O_3–CaO	5.1	98.9	28.3	19.5	11.6	31.1	12.6	8.8	3.7	71.2
3 wt% K_2O/Y_2O_3–CaO	3.8	99.6	37.1	13.5	10.9	24.4	27.2	9.0	10.1	47.3

[a] Reaction conditions: $CH_4/O_2/C_7H_8/H_2O/He = 25/4/2.5/19/5.5$ ml min^{-1}; $T = 700$ °C; catalyst weight = 1.0 g. [b] Content of Y_2O_3 in Y_2O_3–CaO is 10 mol%. [c] Selectivity is calculated on the basis of moles C_7H_8 converted: C_7H_8, C_6H_6, C_8H_{10}, and C_8H_8 denote toluene, benzene, ethylbenzene, and styrene, respectively. [d] $C_8/(C_6 + C_8) \times 100$.

reaction, but were scarcely formed on the other catalysts containing alkali metal oxides. Further, the selectivities to the methylated products on the Y_2O_3–CaO and the PbO–MgO catalysts were lower than those on the catalysts containing alkali metal oxides, except for the Li_2O/SiO_2. These results suggest that existence of alkali metal oxides on the basic materials is essential for the reaction. Among the catalysts tested, the 3 wt% Li_2O/10 mol% Y_2O_3–CaO and the 7 wt% Li_2O/MgO gave the highest yields of the methylated products (>10%), and exhibited little activity in the production of benzene, which is a demethylated product of toluene. The order of the selectivity to the methylated compounds, $Li_2O > Na_2O > K_2O$, was obtained for the alkali metal oxides on 10 mol% Y_2O_3–CaO. The ratio of the methylated products to the methylated and demethylated products (benzene, ethylbenzene, and styrene) on the Na_2O/Y_2O_3–CaO was close to that on the Li_2O/Y_2O_3–CaO, whereas that on the K_2O/Y_2O_3–CaO was extremely low, *i.e.*, benzene was produced as much as the methylated components. This tendency was also observed on $K_2O/BaCO_3$.

We examined the oxidative coupling of methane over 3 wt% Li_2O, Na_2O, and K_2O supported on 10 mol% Y_2O_3–CaO in order to demonstrate the mechanistic correlation with the oxidative methylation of toluene. The reaction was performed in a flow reactor with 0.5 g of the catalyst at 700 °C and the following flow rates, $CH_4/O_2/He = 12.5/2/13.5$ ml min^{-1}. The selectivities to C_{2+} hydrocarbons (C_2H_6, C_2H_4, C_3H_8, and C_3H_6) over Li_2O, Na_2O, and K_2O on Y_2O_3–CaO were 60.6, 52.4, and 45.9%, respectively. This order was compatible with the order for the oxidative methylation of toluene with methane, suggesting that the formation of a new C–C bond for the oxidative methylation of toluene depended on the reaction between a methyl radical and a benzyl radical. It may be assumed that once the benzyl radical is formed on the basic surface of the catalyst, it reacts and recombines immediately with the methyl radical, which is present in large quantities near the surface, to form the methylated compounds (mainly ethylbenzene rather than xylenes).

Thus, the catalysts containing alkali metal oxides and basic oxides, particularly Li_2O/Y_2O_3–CaO, were active and selective for the oxidative methylation of toluene with methane to form ethylbenzene and styrene without formation of carbonaceous deposits. The selectivity to the methylated compounds over alkali metal oxides on Y_2O_3–CaO catalysts increased in the order $Li_2O > Na_2O > K_2O$. This order correlates well with the order for the oxidative coupling of methane.

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