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A Selective Formation of Styrene by Oxidative Methylation of Toluene with Methane over a PbO/MgO Catalyst

Yo OSADA,* Nobutaka OKINO, Sadao OGASAWARA, Takakazu FUKUSHIMA,
Tsutomu SHIKADA,† and Takao IKARIYA*†
Department of Materials Science and Chemical Engineering, Faculty of Engineering,
Yokohama National University, Hodogaya-ku, Yokohama 240
†Advanced Technology Research Center, NKK Corporation, Kawasaki-ku, Kawasaki 210

The oxidative methylation of toluene with methane to styrene was studied using a lead oxide supported on magnesia catalyst. Although coke deposits were observed on the catalyst, it was found that a high selectivity of 41% for styrene was stably obtained at 40% toluene conversion over 1g of 20 wt% PbO/MgO catalyst at 973 K.

Styrene is currently manufactured from alkylation of benzene with ethylene followed by dehydrogenation of resulting ethylbenzene. A process for the production of styrene directly from other available sources, such as toluene and methane or methanol, would potentially reduce the cost, and provides a new route for an alternative petroleum feedstock. Oxidative methylation of toluene with methane to ethylbenzene and styrene is one of the promising attempts to provide this need, and a few reports on this reaction have been made.[1-3] Recently we reported that a lithium-promoted Y_2O_3-CaO catalyst showed an excellent catalytic performance for the reaction to form the C_8 aromatics (ethylbenzene and styrene) without producing oxygenated compounds and carbonaceous deposits under a relatively high partial pressure of methane.[4] However, these catalysts exhibited smaller selectivity for styrene than ethylbenzene or other by-products. In this communication we report on the catalytic activity of a PbO/MgO catalyst[5] to this reaction under the high partial pressure of methane.

All catalysts used were prepared by impregnating magnesia with a solution of $Pb(NO_3)_2$ or Li_2CO_3 dissolved in a dilute nitric acid, drying and calcining in air at 1073 K for 6 h. The experiments were carried out using a conventional flow-quartz reactor (12 mm i.d.) packed with 1g of the catalyst. A typical feed gas-flow rates were $CH_4/C_6H_5CH_3/O_2$ = 50/2.5/4 ml min^{-1}NTP at 973 K for 3.5 h. All the products were analyzed by gas chromatography.

Ethylbenzene, styrene, and benzene were obtained as principal aromatic hydrocarbons. After a reaction, coke deposits were observed on some catalysts. Table 1 shows the results of the reaction for the catalysts supported on magnesia. The selectivity to the each product was calculated on the basis of moles toluene converted. The PbO/MgO catalyst exhibited the best yield and selectivity for the production of styrene at 973 K, but coke was deposited on it; nevertheless the

Table 1. Catalytic Performance of Supported Lead Oxides for Oxidative Methylation of Toluene with Methane[a]

Run	Catalyst	Coke	Conversion/%			Selectivity/%[c]				Ratio of
		deposits[b]	CH_4	TL	O_2	(EB+ST)	EB	ST	BZ	ST/EB
1	MgO	●	1.3	17.8	100	7.7	3.0	4.7	15.9	1.57
2	20wt%PbO/MgO	●	4.4	39.6	100	66.4	25.0	41.4	21.3	1.66
3	20wt%PbO/MgO[d]	●	2.1	36.3	100	65.6	25.6	40.0	20.7	1.56
4	20wt%PbO/MgO[e]	●	1.5	33.3	100	26.1	15.1	11.0	21.8	0.73
5	20wt%PbO/MgO[f]	●	2.3	36.1	98.2	50.4	30.3	20.1	21.8	0.66
6	7wt%Li_2O/MgO	○	1.7	15.3	59.1	68.9	53.3	15.6	13.4	0.29
7	7wt%Li_2O-20wt%PbO/MgO	●	0.8	28.7	100	55.6	33.5	22.1	13.9	0.66
8	7wt%Li_2O/20wt%PbO/MgO	●	1.9	33.9	100	49.6	30.1	19.6	11.4	0.65
9	20wt%PbO/7wt%Li_2O/MgO	○	0.6	22.1	95.3	68.1	49.3	18.8	8.9	0.38
10	20wt%PbO/1wt%Li_2O/MgO	●	4.7	23.5	100	66.8	39.7	27.1	18.5	0.68

a) Reaction conditions : $CH_4/C_6H_5CH_3/O_2$ = 50/2.5/4 ml min^{-1}NTP; T = 973 K; catalyst weight = 1.0g; data at 3 h. b) Coke deposits were observed (●), not observed (○). c) Selectivity is calculated on the basis of moles toluene converted: TL, EB, ST, and BZ denote toluene, ethylbenzene, styrene, and benzene, respectively. d) Data at 12 h. e) T = 923 K. f) Catalyst weight = 0.2 g.

decrease in the selectivities was little during the reaction for 12 h. In addition, the initial activity was completely recovered by combustion of the coked catalyst with O_2 diluted with He. At a lower reaction temperature, 923 K, and a short contact time with 0.2g of the catalyst, the selectivity to C_8 compounds decreased and the selectivity to ethylbenzene exceeded that of styrene. From the results described in our previous report on the Y_2O_3-CaO catalyst,[4] the addition of alkali metals to this catalyst prevents the coke formation and improves the C_8 selectivity. Then we examined the effect of the addition of lithium to PbO/MgO. As shown in runs 7 and 8, both the catalysts, which were prepared by a simultaneous wet impregnation of MgO with a mixed solution containing Pb^{2+} and Li^+ and by a stepwise impregnation of the PbO/MgO with a solution of Li_2CO_3, gave not only the coke deposition but also the drop in the C_8 and styrene selectivities. In the case of the catalyst prepared by the addition of 20 wt% PbO to 7 wt% Li_2O/MgO, the coke formation was suppressed and kept the total C_8 selectivity, but the preferential styrene productivity was completely diminished.

In conclusion, the PbO/MgO catalyst was found to have the high catalytic activity and selectivity for the direct production of styrene by oxidative methylation of toluene with methane, irrespective of the coke deposition.

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