Oxidative Methylation of Toluene with Methane over Basic Zeolite Catalysts Promoted with Alkali Metal Bromides and Alkali Metal Oxides

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Abstract: The catalytic effects for the oxidative methylation of toluene with methane over the basic zeolite catalysts prepared by promoting KY, KX, KM, KZSM-5 or Kβ with alkali-metal bromides and alkali-metal oxides have been investigated comparatively. The alkali-metal bromides promoted substrates are more effective than the alkali-metal oxides promoted systems. Moreover, the NaBr promoted systems are more active than KBr promoted systems. The most effective catalytic system (8wt%NaBr)/KZSM-5 gave a toluene conversion as high as 76.3% and a total C_8 selectivity of 76.4% (styrene/ethylbenzene=9.76) resulting in a total C_8 yield of 58.3%.

Keywords: Styrene, methane, oxidative methylation, alkali-metal oxides, alkali-metal bromides.

Introduction

Styrene is one of the most important industrial monomers. At present, styrene is mainly produced by alkylation of benzene with ethylene followed by oxidative dehydrogenation of the resulting ethylbenzene. However, this process is very expensive and complex. A new method of synthesizing ethylbenzene and styrene directly from toluene and methane was discovered by Khcheyan *et al.*[1], and Yakovich and Bakareva[2]. The process would potentially reduce the cost because of the production of styrene directly from toluene and methane. Recently, several research groups have employed some metal oxides for the oxidative methylation of toluene with methane[3-6].

It is known that zeolite is the focus of the catalytic chemistry. In contrast to extensive studies of acidity and acid catalysis of zeolite, less attention has been given to the studies of base catalysis of zeolite. Applying basic zeolite to the oxidative methylation of toluene with methane is a new field which has potential economic effect and great theoretical value. In this communication, alkali metal exchanged zeolites have been used in the oxidative methylation of toluene with methane. It was found that these basic zeolites were effective catalyst for the oxidative methylation of toluene with methane.

Experimental

Catalyst preparation

Zeolite NaY and NaX raw powder was obtained from Chemical plant of Wenzhou, Zeolite NaZSM-5 raw powder was obtained from Chemical plant of Nankai University, Zeolite NaM and Naβ raw powder was obtained from Chemical plant of Fushun. Sample KX, KY, KM, KZSM-5 and Kβ were prepared from NaX, NaY, NaM, NaZSM-5 and Naβ raw powder respectively by exchanging with 0.5mol/L KNO_3 aqueous solution at 358K for 2h. The exchange procedures were repeated four times. On completion of four times exchange, the sample was filtered and washed with deioned water. The sample was then dried at 398K followed by calcining in air at 773K for 5h. Loaded catalysts were prepared by impregnating aqueous solution of $LiNO_3$, NaBr and Cs_2O onto KY zeolite described above respectively. Each catalyst was calcined in air at 773K for 5h. The powdered catalyst was made into pellets, crushed, and then sieved (40-60mesh).

Catalyst screening and product analysis

The experiments in this work were carried out using a conventional fixed bed flow-type quartz reactor (6-mm i.d.). The typical experimental conditions were as follows: reaction temperature = 973K, CH_4 flow rate =24mL / min, toluene flow rate = 2.33 mL / min, weight of catalyst/total feed rate (W/F) = 2.14g.h/mL. CH_4 / O_2 / $C_6H_5CH_3$ / N_2 (diluent) = 24:6:2.33:20 ml/min. Toluene was introduced by passing the reactant gas mixture into a toluene vapor saturator just before the inlet of reactor. Liquid products were trapped in an ice-salt bath, and were analyzed by gas chromatography using a SE-30 capillary column with flame ionization detection (FID). The main products were styrene, ethylbenzene, benzene, trace amounts of xylenes, and water.

Results and discussion

Table 1 shows the results of the reaction for the oxidative methylation of toluene with methane over modified zeolite catalysts at 973K. Effects of additive alkali metal oxides and alkali metal bromides over KY zeolite on the toluene conversion, C_8 yield and C_8 selectivity were first examined. Among these alkali metal oxides and alkali metal bromides tested, alkali metal bromides promoted KY are more effective catalytic systems than alkali metal oxides promoted KY. Moreover, the ratios of styrene to ethylbenzene on alkali metal bromides promoted KY catalyst are larger than that of alkali metal oxides promoted KY catalysts. The results which are presented in **Table 1** show that the toluene conversion decreased in the following order: NaBr/KY > KBr/KY > Cs_2O/KY > K_2O/KY > Na_2O/KY > NaCl/KY > Li_2O/KY, the yield of C_8 compounds (ethylbenzene + styrene) decreased in the following order: NaBr/KY > KBr/KY > Cs_2O/KY > Na_2O/KY~ NaCl/KY > K_2O/KY > Li_2O/KY and the selectivity of C_8 compounds (ethylbenzene + styrene) decreased in the following order: NaBr/KY > KBr/KY > NaCl/KY > Li_2O/KY > Cs_2O/KY > Na_2O/KY > K_2O/KY. In addition, from the results which are summarized in **Table1**, it was also found that the selectivity of benzene on alkali metal oxides promoted KY catalyst is larger than that of alkali metal bromides promoted KY catalysts.

Table 1. Oxidative Methylation of Toluene with Methane over Modified Zeolite Catalysts [a]

Catalyst	Conversion (mol%) C_7H_8[b]	Selectivity(%)				ST/EB[g]	Yield(%)			
		C_6H_6[c] (BZ)	C_8H_{10}[d] (EB)	C_8H_8[e] (ST)	Total C_8[f] (ST+EB)		C_6H_6 (BZ)	C_8H_{10} (EB)	C_8H_8 (ST)	Total C_8 (ST+EB)
Li_2O/KY	25.5	28.1	32.3	25.8	58.1	0.80	7.2	8.2	6.6	14.8
Na_2O/KY	37.5	31.5	28	21.6	49.6	0.77	11.8	10.5	8.1	18.6
K_2O/KY	38.4	40.1	26.1	16.9	43	0.65	15.4	10	6.5	16.5
Cs_2O/KY	57.1	40.0	15.9	36.4	52.3	2.29	9.1	9.1	20.8	29.9
NaCl/KY	29.6	14.2	40.6	22.4	63	0.55	4.2	12	6.60	18.6
NaBr/KX	65.0	11.8	11.3	64.4	75.7	5.70	7.7	7.4	41.9	49.3
NaBr/KY	65.0	7.5	8.3	73.4	81.7	8.84	4.9	5.4	47.7	53.1
NaBr/KM	62.0	11.2	10.8	68.0	78.8	6.30	6.9	6.7	42.2	48.9
NaBr/ KZSM5	76.3	9.9	7.1	69.3	76.4	9.76	7.6	5.4	52.9	58.3
NaBr/Kβ	61.7	16.7	7.1	68.7	75.8	9.68	10.3	4.4	42.4	46.8
KBr/KX	52.2	21.5	18.1	46.8	64.9	2.59	11.2	9.5	24.4	33.9
KBr/KY	58.9	14.8	17.9	51.0	68.9	2.85	8.7	10.5	30.0	40.5
KBr/KM	57.4	16.3	16.1	56.4	72.5	3.5	9.4	9.2	32.4	41.6
KBr/ KZSM5	58.2	15.6	13.6	58.6	72.2	4.31	9.1	7.9	34.1	42.0
KBr/Kβ	60.1	14.0	13.3	58.0	71.3	4.36	8.4	8.0	34.9	42.9

Note: a. T_R= 973K, W=0.3g, $CH_4/O_2/C_6H_5CH_3/N_2$ =24:6:2.33:20(mL/min).The results presented were obtained after 2h of reaction. The yield is on the basis of moles of toluene converted
b. toluene c. benzene d. ethylbenzene e. styrene f. ethylbenzene + styrene
g. ST/EB = selectivity ratio of styrene to ethylbenzene.

Secondly, the effects of different zeolites promoted with alkali metal bromides were compared. The results showed that NaBr promoted systems were more effective than KBr promoted systems. Among NaBr promoted systems, NaBr promoted KZSM-5 gave the highest C_8 yield of 58.3% with the C_8 selectivity of 76.4% [styrene/ethylbenzene = 9.76(mol)]. The rest four-type zeolites promoted with NaBr showed the similar toluene conversion, C_8 yield and C_8 selectivity. Comparing the effects of different zeolites promoted with KBr, the results presented in **Table 1** showed that the KBr/KZSM-5 and KBr/Kβ catalyst showed similar catalytic performance for the oxidative methylation of toluene. The toluene conversion and C_8 Yield and C_8 selectivity of KBr/KY catalyst was also similar to that of KBr/KZSM-5 and KBr/Kβ catalysts. The lowest performance was exhibited by KBr/KX with a total C_8 selectivity of 64.9% and C_8 yield of 33.9%.

In conclusion, the basic zeolites are effective catalysts for the oxidative methylation of toluene with methane. The alkali-metal bromides promoted substrates are more effective than the alkali-metal oxides promoted systems. Moreover, the NaBr promoted systems are more effective than KBr promoted systems.

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