Chinese Chemical Letters Vol. 13, No. 9, pp 911 – 914, 2002
http://www.imm.ac.cn/journal/ccl/html 

# Studies of the Effects of Alkali Metal Oxides Promoter on the Oxidative Methylation of Toluene with Methane over KY Zeolite Catalysts

Ling Ping ZHOU[1]*, Wei LI[2], He Xuan LI[2], Ke Yi TAO[2]

[1]College of Chemistry and Molecular Engineering, Perking University, Beijing 100871
[2]Department of Chemistry, Nankai University, Tianjin 300071

**Abstract :** The toluene conversion, the selectivity to styrene and ethylbenzene( $C_8$ selectivity) in the oxidative methylation of toluene with methane have been studied comparatively for the KY zeolite catalyst promoted with $Li_2O$, $Na_2O$, $K_2O$, and $Cs_2O$ respectively. It was found that the effect of promoter decreased in the order: $Cs_2O$>$Na_2O$>$Li_2O$>$K_2O$.

**Keywords :** KY zeolite, oxidative methylation, toluene, methane.

Methane is the most abundant component of natural gas. The direct conversion of methane into chemical feedstock or transportable liquid fuel is an attractive process. In addition to oxidative coupling of methane, oxidative methylation of toluene with methane to styrene and ethylbenzene which has been investigated by Khcheyan *et al.*[1], provides another possibility of methane utilization. Recently, several research groups have employed some metal oxides for the oxidative methylation of toluene with methane[2-6]. 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 article, K- exchanged Y zeolites promoted with alkali metal oxides have been used in the oxidative methylation of toluene with methane. It was found that these basic zeolites were effective catalysts for the oxidative methylation of toluene with methane.

## Experimental

*Catalyst preparation* Zeolite NaY raw powder was obtained from chemical plant of Wenzhou. Sample KY was prepared from NaY raw powder by exchange with 0.5 mol/L $KNO_3$ aqueous solution at 358 K. The exchange procedures were repeated four times.

---

*E-mail: zhou_ling_ping@hotmail.com

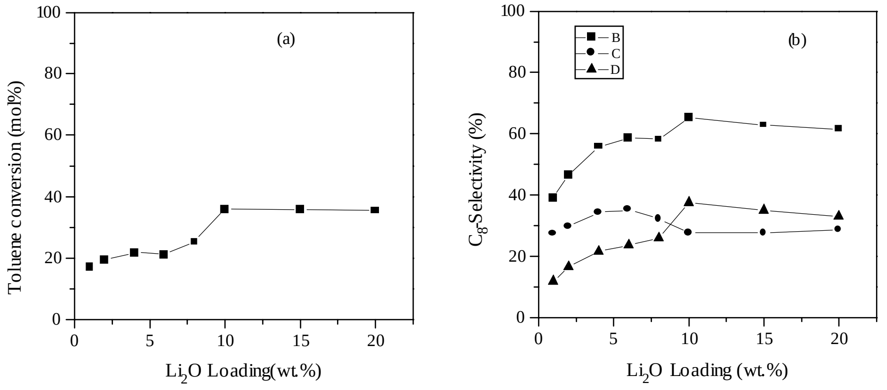
The time of each exchange was 2 h. On completion of four times exchange, the sample was filtered and washed with deioned water. The sample was then dried at 398 K followed by calcination in air at 773 K for 5 h. Loaded catalysts were prepared by impregnating aqueous solution of $LiNO_3$, $NaNO_3$, $KNO_3$ and $CsNO_3$ onto KY zeolite respectively. Each catalyst was calcined in air at 773 K for 5 h. The powdered catalyst was made into pellets, crushed, and then sieved (40-60mesh).

*Catalyst screening and product analysis* The experiments were carried out using a conventional fixed bed flow type quartz glass reactor (6 mm i.d.). The typical experimental conditions were as follows: reaction temperature = 973 K, $CH_4$ flow rate = 24 ml/min, toluene flow rate = 2.33 ml/min (g), weight of catalyst / total feed rate (W / F) = 2.14 g.h./mol. $CH_4$ / $O_2$ / $C_6H_5CH_3$ / $N_2$ (diluent) = 24: 6: 2.33: 20 ml.min$^{-1}$. Toluene was introduced by passing the reactant gas mixture into a toluene vapor saturator equipped just before the inlet of reactor. Liquid products condensed in an ice-salt bath were analyzed by gas chromatography using a SE-30 capillary column with flame ionization detection (FID). The main products were styrene, ethylbenzene, benzene and trace amounts of xylene, water.

## Results and Discussion

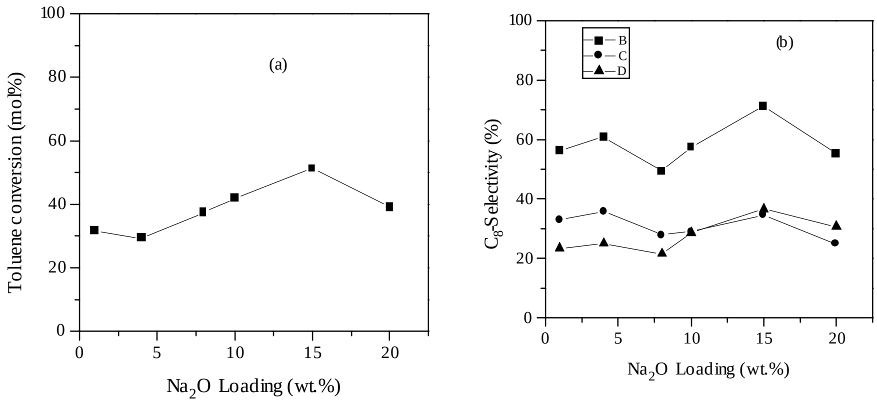
*Effects of $Li_2O$ loading* The effect of $Li_2O$ loading on the KY catalyst has been investigated. **Figures 1(a)** and **1(b)** present the effect of the $Li_2O$ loadings on the performances(toluene conversion and $C_8$-selectivity) of the resulting catalysts. The $Li_2O$ loadings were varied from 1 to 20 wt.% for the $Li_2O$-promoted KY systems. With the increase in $Li_2O$ loadings, the toluene conversion increased slowly, when $Li_2O$ loadings higher than 10 wt.% $Li_2O$ /KY, the toluene conversion remained almost constant. With the increase of $Li_2O$ loadings the total $C_8$-selectivity also increased, when $Li_2O$ loadings higher than 8wt.% $Li_2O$ /KY, the total $C_8$-selectivity remained almost unchanged. But, a prominent difference between the EB-selectivity and ST-selectivity was observed with the increase of $Li_2O$ loadings.

**Figure 1** Effects of $Li_2O$ loading on the toluene conversion (a) and the $C_8$ selectivity (b). [ (B) Total $C_8$, (C) Ethylbenzene, (D) Styrene ]



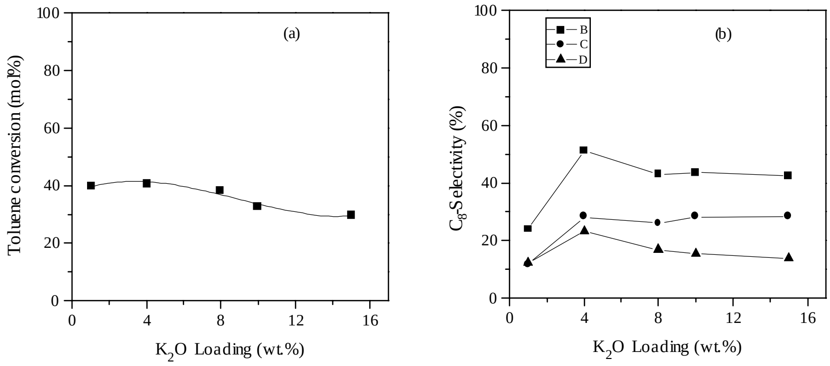
*Effects of $Na_2O$ loading* **Figure 2(a)** and **2(b)** showed the toluene conversion and the $C_8$ selectivities at 973 K with variation in the loading level of $Na_2O$ on KY. The toluene conversion increased slightly with the increase of $Na_2O$ loadings. The catalyst containing 15 wt.% $Na_2O$ exhibited the maximum toluene conversion (51%) and total $C_8$-selectivity (66%). The toluene conversion and the total $C_8$-selectivity slightly decreased with further increase in the amount of $Na_2O$. However, the changes of the EB-selectivity and the ST-selectivity showed different, the ST-selectivity exhibited the similar changes as the total $C_8$-selectivity, while the EB-selectivity slightly decreased with the increase of $Na_2O$ loadings.

**Figure 2** Effects of $Na_2O$ loading on the toluene conversion (a), the $C_8$ selectivity (b). [ (B) Total $C_8$, (C) Ethylbenzene, (D) Styrene ]



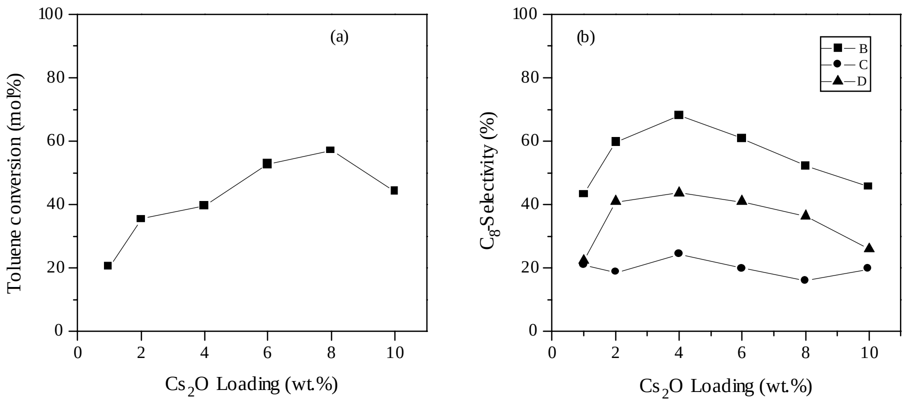

*Effects of $K_2O$ loadings* Effects of $K_2O$ loading on toluene conversion and $C_8$-selectivities are shown in **Figure 3(a)** and **3(b)**. With increasing amount of $K_2O$ loading, the toluene conversion slightly decreased. The total $C_8$-selectivity and ST-selectivity increased attaining (51%) and (23%) respectively at a loading of 6 %wt $K_2O$, followed by a slight decrease. In contrast, with the increase in the $K_2O$ loadings the EB selectivity continued to increase, remaining almost unchanged with further increase.

**Figure 3** Effects of $K_2O$ loading on the toluene conversion (a) and the $C_8$ selectivity (b). [ (B) Total $C_8$, (C) Ethylbenzene, (D) Styrene]



*Effects of $Cs_2O$ loading* Effects of $Cs_2O$ loading on the toluene conversion and the $C_8$ selectivity are presented in **Figure 4(a)** and **4(b)**. **Figure 4(a)** shows that the toluene conversion increases as the $Cs_2O$ loading increases from 1% to 10%. The catalyst containing 8wt% $Cs_2O$ exhibited the maximum toluene conversion (56%). Further increases in the amount of $Cs_2O$ decreased the toluene conversion. With increasing $Cs_2O$ loading, the total $C_8$-selectivity increases, passing through a maximum (68%) at a loading of 4wt.% $Cs_2O$ followed by some decreases (**Figure 4b**). A noticeable difference between the EB-selectivity and ST-selectivity was observed with increasing $Cs_2O$ loading. The ST-selectivity showed the similar change trend as the total $C_8$-selectivity while the EB-selectivity slowly decreases with the increase of $Cs_2O$ loadings.

**Figure 4** Effects of $Cs_2O$ loading on the toluene conversion (a) and the $C_8$ selectivity(b). [(B) Total $C_8$, (C) Ethylbenzene, (D) Styrene]




By comparing **Figure1(a)**, **Figure 2(a)**, **Figure 3(a)** and **Figure 4(a)** the results suggest that proper addition of $Li_2O$, $Na_2O$, $Cs_2O$ is effective for increasing the toluene conversion. In contrast, with increasing amount of $K_2O$ loading, the toluene conversion is decreases in the following order: $Cs_2O$> $Na_2O$>$Li_2O$>$K_2O$. By comparing **Figure1(b)**, **Figure 2(b)**, **Figure 3(b)** and **Figure 4(b)**, the $C_8$-selectivity has a maximum which suggests that it exists the best value for the alkali metal oxides loadings. The $C_8$-selectivity is decreased in the following order: $Cs_2O$> $Na_2O$>$Li_2O$>$K_2O$. In terms of the toluene conversion and the $C_8$-selectivity, the following sequence was observed for the effect of promoter: $Cs_2O$> $Na_2O$>$Li_2O$>$K_2O$.

## Acknowledgment

This work was supported by the National Natural Science Foundation of China, Grant No.: 29803005 and 29673022.

## References

1. Kh. E. Khcheyan, A. N. Shatalova, O. M. Revenko, *et al.*, *Nertekhimiya*, **1980**, *20*, 876.
2. T. Suzuki, K. Wada, Y. Watanabe, *Appl. Catal.*, **1989**, *53*, L19.
3. Y. Osada, K. Enomoto, T. Fukushima, *et al.*, *J. Chem. Soc. Chem. Commun.*, **1989**, *1156*.
4. T. Suzuki, K. Wada, Y. Watanabe, *Ind. Eng. Chem. Res.*, **1991**, *30*, 1719.
5. H. Kim, M. S. Hyung, P. Hangnam, *Appl. Catal. A*, **1992**, *87*, 115.
6. A. Z. Khan, E. Ruckenstein, *Appl. Catal. A*, **1993**, *102*, 233.

Received 27 December, 2001