JOURNAL OF CATALYSIS **150**, 430–433 (1994)

# NOTE

# Selective Para Chlorination of *o*-Xylene over Zeolite Catalysts

The production of 4-chloro-*o*-xylene (4-Cl-*o*x) in high selectivity is important due to its usefulness in the production of intermediates for thermoplastics, pharmaceuticals and agrochemicals. Chlorination of *o*-xylene has long been investigated using Lewis acid catalysts such as $AlCl_3$, $FeCl_3$, and $SbCl_5$ (1–4). These catalysts also produce a large amount of less valuable products like 3-chloro-*o*-xylene (3-Cl-*o*x) and poly-substituted chloro products. In recent years, some studies on the selective halogenation of aromatic compounds over basic zeolites have been reported (5–9). However, the development and utilization of base catalysis of zeolites are still limited. The objective of the present work is to chlorinate the *o*-xylene at the para position in high yields using basic zeolite catalysts. In the present note, we describe the results of the influence of various zeolites, solvents, reaction temperature, and cation exchange on the para selectivity in the liquid phase chlorination of *o*-xylene. The results obtained over different catalysts are compared with that of the conventional catalysts, $FeCl_3$ and silica gel. To prove the generality of the reaction, the chlorination of *m*-xylene and *p*-xylene over the basic K–L zeolite is also reported in this paper.

Zeolites type L, beta, and ZSM-5 were synthesized according to literature procedures (10–12). Na–Y, Na–X, and H–mordenite were obtained from Laporte Inorganics, Cheshire, U.K. The procedure for cation exchange in these zeolites has been reported elsewhere (7). The cationic contents and silicon-to-aluminum ratios of these catalysts (Table 1) were analyzed using an atomic absorption spectrometer (Hitachi Z-800). X-ray diffraction patterns showed that the crystal structures of the zeolites were undamaged after exchange. The catalysts were activated at 165°C (12 h) prior to the reaction.

Anhydrous and AR grade chemicals were used without further purification. The reaction between *o*-xylene and gaseous chlorine was carried out in a 150-ml three-necked flask attached to a condenser, $N_2$/or $Cl_2$ gas line, and septum used to sample the reaction mixture. The temperature of the reaction vessel was maintained using an oil bath. In a typical run, *o*-xylene (0.08 mol) in 30 ml solvent was added to the activated zeolite (1.6 g). The reaction mixture was magnetically stirred and heated to the required temperature at atmospheric pressure under nitrogen flow. The nitrogen gas was stopped and chlorine gas was passed at a rate of 0.04 mol/h. The chemical analysis of the products was performed in a gas chromatograph (HP5890 series II) equipped with a flame ionization detector and a capillary column (50 m × 0.2 mm i.d.) coated with methyl silicon gum. Reactants and products were identified by reference to standards.

The main catalytic properties of the different catalysts in the chlorination of *o*-xylene are reported in Table 1. In order to examine the yield difference for 4-Cl-*o*x, the catalysts are compared at nearly similar levels of conversion and under identical conditions. The isomer distribution (4-Cl-*o*x/3-Cl-*o*x) obtained using a conventional catalyst, $FeCl_3$, is also included (Table 1) for comparison. A wide variety of products is obtained. The major ones are 4-chloro-*o*-xylene and 3-chloro-*o*-xylene. 2-methyl benzyl chloride (2-MBC) and polychlorinated-*o*-xylenes (others) such as di-, tri-, and tetrachloro-*o*-xylenes were also observed in differing yields in the product, depending on the type of catalyst and operating conditions. Similar products have been reported by Lanchec and Blouri (13) in the chlorination of *o*-xylene using chlorine gas and various solvents in the absence of any catalyst.

Various zeolites have been studied to ascertain their yields for 4-Cl-*o*x. The formation of 3- and 4-Cl-*o*x (monochloro-*o*-xylenes) takes place by parallel reactions (5). The di-, tri-, and tetrachloro-*o*-xylenes are obtained by secondary consequitive reactions (5) of the monochloro-*o*-xylenes. A small amount of 2-MBC is probably produced by the photochlorination of $CH_3$ group of *o*-xylene (14). The results show a strong influence of different catalysts on the yield of 4-Cl-*o*x and 4-Cl-*o*x/3-Cl-*o*x selectivity in the chlorination of *o*-xylene, the yields varying from 16.1 to 35.2% and the selectivities varying from 1.0 to 11.73. In the present study, zeolite K–L exhibited the highest 4-Cl-*o*x/3-Cl-*o*x selectivity (11.73) when compared to the other catalysts. The results obtained over K–L zeolite are significantly higher compared to the $FeCl_3$ catalyst (Table 1). The maximum yield of 2-MBC was obtained in the absence of any catalyst, which may be attributed to the photochlorination of the side chain of

0021-9517/94 $6.00

TABLE 1

**Chlorination of *o*-Xylene over Various Zeolites**[a]

| Catalyst | $SiO_2/Al_2O_3$ molar ratio | Degree of $K^+$-exchange in zeolites (wt%)[b] | Uncoverted *o*-xylene (wt%) | Yields (wt%)[c] | | | | 4-Cl-*ox*/3-Cl-*ox* isomer ratio |
|---|---|---|---|---|---|---|---|---|
| | | | | 4-Cl-*ox* | 3-Cl-*ox* | 2-MBC | Others | |
| No catalyst | — | — | 61.6 | 13.2 | 10.7 | 5.2 | 9.3 | 1.2 |
| Silica gel | — | — | 65.2 | 19.7 | 13.8 | 0.2 | 1.1 | 1.43 |
| $FeCl_3$ | — | — | 61.2 | 16.1 | 16.1 | — | 6.6 | 1.00 |
| K-ZSM-5 | 41.0 | 96.0 | 63.3 | 20.3 | 14.1 | 0.3 | 2.0 | 1.44 |
| K-Y | 4.1 | 92.8 | 59.2 | 21.2 | 14.2 | 0.6 | 4.8 | 1.49 |
| K-mordenite | 22.0 | 89.8 | 57.7 | 24.5 | 15.8 | 0.3 | 1.7 | 1.55 |
| K-beta | 32.7 | 85.9 | 59.8 | 24.0 | 14.7 | 0.4 | 1.1 | 1.63 |
| K-X | 2.4 | 92.6 | 58.8 | 17.3 | 9.8 | 3.8 | 10.3 | 1.76 |
| H.K-L | 6.3 | 23.4 | 56.5 | 23.0 | 17.9 | 0.3 | 2.3 | 1.28 |
| K-L | 6.3 | 98.6 | 60.6 | 35.2 | 3.0 | 0.1 | 1.1 | 11.73 |

[a] Reaction conditions: catalyst = 21.2 g/mol *o*-xylene; reaction temperature = 80°C; *o*-xylene = 0.08 mol; solvent ($ClCH_2CH_2Cl$) = 30 ml; $Cl_2$ flow = 0.04 mol/h.

[b] Degree of $K^+$-exchange (%) = 100 x moles of K/moles of Al.

[c] 4-Cl-*ox*, 4-chloro-*o*-xylene; 3-Cl-*ox*, 3-chloro-*o*-xylene; 2-MBC, 2-methyl benzyl chloride; others, polychlorinated-*o*-xylenes (di-, tri-, and tetra-chloro-*o*-xylenes).

*o*-xylene (14). The 4-Cl-*ox*/3-Cl-*ox* selectivities over $FeCl_3$ and silica gel, and in the absence of any catalyst, were found to be 1.0, 1.43, and 1.23, respectively. The lower isomer ratio of 4-Cl-*ox*/3-Cl-*ox* observed over K-ZSM-5 in the liquid phase chlorination of *o*-xylene may be attributed to the slower diffusion of *o*-xylene (due to its large size, 0.74 nm) in the K-ZSM-5 channels (15). Hence, mostly the reaction is restricted to the catalyst surface. These results are in good agreement with the results obtained over silica gel.

Due to steric restrictions and electrostatic field gradients inside zeolite pores, these are expected to lead to greater para selectivity than $FeCl_3$ or silica gel. However, the results obtained in the liquid phase chlorination of *o*-xylene (inside the zeolite channels) over different zeolites may not be due to geometry-related shape selectivity alone (Table 1) (5, 8, 16).

The catalysts used in this study could be arranged in the decreasing order of their 4-Cl-*ox*/3-Cl-*ox* selectivity as follows:

$$\text{K-L} > \text{K-X} > \text{K-beta} > \text{K-mordenite} > \text{K-ZSM-5} \approx \text{Silicagel} > \text{H.KL} > \text{No catalyst} > FeCl_3.$$

The influence of polarity of various solvents ($ClCH_2CH_2Cl$, $CHCl_3$, $CCl_4$) was studied in the chlorination of *o*-xylene over zeolite K-L at 40°C. The results are summarized in Table 2. An increase in the polarity

TABLE 2

**Influence of Solvent in the Chlorination of *o*-Xylene over K-L Zeolite**[a]

| Solvent | Reaction temperature (°C) | Unconverted *o*-Xylene (wt%) | Yields (wt%)[b] | | | | 4-Cl-*ox*/3-Cl-*ox* isomer ratio |
|---|---|---|---|---|---|---|---|
| | | | 4-Cl-*ox* | 3-Cl-*ox* | 2-MBC | Others | |
| $ClCH_2CH_2Cl$ | 80 | 60.6 | 35.2 | 3.0 | 0.1 | 1.1 | 11.73 |
| $ClCH_2CH_2Cl$ | 40 | 58.3 | 26.7 | 10.3 | 0.2 | 4.5 | 2.59 |
| $CHCl_3$ | 40 | 58.8 | 26.6 | 11.3 | 0.4 | 2.9 | 2.35 |
| $CCl_4$ | 70 | 58.6 | 30.4 | 8.4 | 0.3 | 2.3 | 3.61 |
| $CCl_4$ | 40 | 58.0 | 21.3 | 15.9 | 0.5 | 4.3 | 1.34 |
| No Solvent[c] | 80 | 56.8 | 24.5 | 12.1 | 5.3 | 1.3 | 2.02 |
| No Solvent[c] | 40 | 55.6 | 24.6 | 12.9 | 3.8 | 3.1 | 1.91 |

[a] Reaction conditions as in Table 1.

[b] Abbreviations as in Table 1.

[c] Reaction conditions: catalyst = 5.7 g/mol *o*-xylene; *o*-xylene = 0.28 mol; $Cl_2$ flow = 0.04 mol/h.

TABLE 3

**Influence of Various Cation-Exchanged L Zeolites in the Chlorination of *o*-Xylene at 80°C[a]**

| | Cation composition(%)[b] | | | Uncoverted *o*-xylene (wt%) | Yields (wt%)[c] | | | | 4-Cl-*o*x/3-Cl-*o*x isomer ratio |
|---|---|---|---|---|---|---|---|---|---|
| Zeolite | $H^+$ | $K^+$ | $M^{+n}$ | | 4-Cl-*o*x | 3-Cl-*o*x | 2-MBC | Others | |
| H.K–L | 75.6 | 23.5 | 0.9 | 56.5 | 23.0 | 17.9 | 0.3 | 2.3 | 1.28 |
| Li.K–L | — | 19.5 | 80.5 | 45.6 | 31.1 | 19.9 | 0.9 | 2.5 | 1.56 |
| Na.K–L | — | 21.2 | 78.8 | 53.9 | 30.3 | 13.6 | 0.8 | 1.4 | 2.23 |
| K–L | — | 98.6 | 1.4 | 60.6 | 35.2 | 3.0 | 0.1 | 1.1 | 11.73 |
| Ca–K–L | — | 17.3 | 82.7 | 55.1 | 25.4 | 17.8 | 0.2 | 1.5 | 1.43 |
| Sr–K–L | — | 20.8 | 79.2 | 56.5 | 26.0 | 15.9 | 0.3 | 1.3 | 1.63 |
| Ba–K–L | — | 22.5 | 77.5 | 56.1 | 25.6 | 16.4 | 0.6 | 1.3 | 1.56 |
| Ag–K–L | — | 21.7 | 78.3 | 56.3 | 24.1 | 17.1 | 0.8 | 1.7 | 1.41 |

[a] Reaction conditions as in Table 1.

[b] $M^{+n}$ = Li, Na, Ca, Sr, Ba, and Ag; *n* (valency) = 1 or 2; degree of cation exchange (%) = 100 × moles of $K^+$ + $M^{+n}$/moles of Al. $H^+$ was obtained by determining the difference between the moles of Al and the sum of the moles of $K^+$ and $M^{+n}$ values.

[c] Abbreviation as in Table 1.

of the solvent increases the 4-Cl-*o*x/3-Cl-*o*x ratio. The selectivity for *p*-isomer (4-Cl-*o*x/3-Cl-*o*x ratio) in the absence of any solvent was found to be 1.91.

An increase in the reaction temperature increases the 4-Cl-*o*x/3-Cl-*o*x ratio in $ClCH_2CH_2Cl$ and $CCl_4$ solvents (Table 2). The higher 4-Cl-*o*x/3-Cl-*o*x (11.73) selectivity was obtained for the first time with the use of 1,2-dichloroethane as a solvent using K–L at 80°C.

Influence of the nature of the cation exchanged in the zeolite K–L on the para substitution in *o*-xylene was studied and the results are shown in Table 3. The most acidic H.K–L gave lower para selectivity for 4-Chloro-*o*-xylene compared with other cation-exchanged catalysts (Table 3). The 4-Cl-*o*x/3-Cl-*o*x ratio over alkali (except K–L), alkaline–earth, and Ag-exchanged zeolite L was found to be between 1.41 and 2.23, though K–L showed outstanding *p*-selectivity in the chlorination of *o*-xylene. The reason for this excellent para selectivity is not known. The size and position of K in the zeolite structure may be the factors responsible for the greater para selectivity (4-chloro-*o*-xylene).

The generality of the nuclear chlorination of xylenes (*o*-xylene, *m*-xylene, and *p*-xylene) was investigated in the presence of 1,2-dichloroethane using zeolite K–L at 80°C. The results are listed in Table 4. The nuclear substitution of the xylenes leads to high yields of monochlorinated products. A small amount of methyl benzyl chloride was detected from the corresponding xylenes. 4-chloro-*m*-xylene(4-Cl-*m*x) and 2-chloro-*m*-xylene(2-Cl-*m*x) were the major reaction products in the chlorination of *m*-xylene; however, the chlorination of *p*-xylene gave only a single monochlorinated product, 2-chloro-*p*-xylene(2-Cl-*p*x). The measured product ratios of 4-Cl-*o*x/3-Cl-*o*x and 4-Cl-*m*x/2-Cl-*m*x at nearly 40% conversion levels of xylenes were found to be 11.73 and 6.58, respectively. In the present study, the selective nuclear chlorination of the xylenes proves the generality of the reaction.

TABLE 4

**Chlorination of Xylenes over Zeolite K–L in the Presence of 1,2-Dichloroethane[a]**

| | Xylenes | | |
|---|---|---|---|
| | *o*-Xylene | *m*-Xylene | *p*-Xylene |
| Unconverted xylenes (wt%) | 60.6 | 61.3 | 58.1 |
| | Yields (wt%)[b] | | |
| 4-Cl-*o*x | 35.2 | — | — |
| 3-Cl-*o*x | 3.0 | — | — |
| 2-MBC | 0.1 | | — |
| 4-Cl-*m*x | — | 32.9 | — |
| 2-Cl-*m*x | — | 5.0 | — |
| 3-MBC | — | 0.2 | — |
| 2-Cl-*p*x | — | — | 39.5 |
| 4-MBC | — | — | 0.7 |
| Others | 1.1 | 0.6 | 1.7 |
| | Isomer ratio | | |
| 4-Cl-*o*x/3-Cl-*o*x | 11.73 | — | — |
| 4-Cl-*m*x/2-Cl-*m*x | — | 6.5 | — |

[a] Reaction conditions as in Table 1.

[b] 4-Cl-*mx*, 4-chloro-*m*-xylene; 2-Cl-*m*x, 2-chloro-*m*-xylene; 3-MBC, 3-methyl benzyl chloride; 2-Cl-*p*x, 2-chloro-*p*-xylene; 4-MBC, 4-methyl benzyl chloride; others, polychlorinated xylenes (di-, tri-, and tetrachloro xylenes).

In conclusion, we have shown that 4-chloro-*o*-xylene is produced selectively using zeolite K–L in the chlorination of *o*-xylene. The more polar solvent (1,2-dichloroethane) is found to be a good solvent in increasing the selectivity for 4-chloro-*o*-xylene. A higher 4-Cl-*o*x/3-Cl-*o*x selectivity is obtained by raising the reaction temperature. Cation exchange in zeolite K–L shows that potassium-exchanged zeolite L gave a higher yield of 4-Cl-*o*x. The selective nuclear chlorination of all the xylenes proves the generality of the reactions.

## ACKNOWLEDGMENTS

The authors thank P. Ratnasamy and S. Sivasanker for helpful discussion and encouragement. S. B. K. thanks C. S. I. R., India for research associateship.

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Received January 24, 1994; revised July 6, 1994

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