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NOTE

Selective *para*-Chlorination of Toluene Using Zeolite Catalysts

Chlorotoluenes are used as intermediates in the pesticides, pharmaceutical, peroxide, and other industries. The major use of *para*-chlorotoluene is in the manufacture of *para*-chlorobenzotrifluoride, a key intermediate in dinitroaniline and diphenyl ether herbicides. The conventional Lewis acid catalysts such as $AlCl_3$, $FeCl_3$, or $SbCl_5$ generally give *ortho*- and *para*-substituted compounds, with the *ortho*-isomer frequently exceeding the *para* isomer (1). Although the chlorination of toluene over Lewis acid catalysts in the presence of sulfur compounds has been reported to result in a high *para*-regioselectivity, these methods tend to give lower yields and also lead to di- and tri-substitution (2). Relatively little attention has been paid to the use of zeolites in the field of aromatic halogenation. Recently, some papers and patents have appeared on the liquid-phase halogenation of aromatic compounds using zeolite catalysts (3–7). The zeolite catalysts, particularly L-type, shift the isomer ratio significantly toward *para*-substitution. The objective of the present work is to chlorinate the toluene at *para* position in high yield. We report herein briefly the results of the influence of various zeolites, monochloroacetic acid (a co-catalyst), reaction temperature, and solvents on the *para*-selectivity in the chlorination of toluene. The results obtained over different catalysts were compared with that of a conventional catalyst, $FeCl_3$. Chlorination of toluene over K–L-type zeolite has not been reported so far in the literature.

Zeolite H-mordenite, Na–Y, Na–X, and K–L were obtained from Laporte Inorganics, Cheshire, U.K. ZSM-5 and Beta zeolites were synthesized as per published procedures (8, 9). These zeolites were converted into their potassium form by repeated exchanges with solution of KNO_3 (1 *M* solution; 10 ml/g zeolite; temperature, 353 K; duration, 6 h; pH = 7–8; three exchanges). Zeolite H K–L was prepared from the K–L by repeated exchanges with ammonium nitrate solution. The procedure adopted was the same as for K-zeolites. The washed zeolites were dried at 383 K for 2 h and calcined at 773 K for 8 h. The chemical analyses of the zeolites were carried out by a combination of wet chemical and atomic absorption (Hitachi Z-800) methods. The properties of zeolites used in this study are presented in Table 1. The zeolite samples were activated at 438 K for at least 2 h before use in the experiments so as to keep dry reaction conditions.

All the chemicals and solvents used were anhydrous and high purity (AnalaR) grade. The catalytic reaction was carried out in a three-necked flask (capacity, 150 ml) fitted with a condenser, gas supply tube, and a septum. The temperature of the reaction vessel was maintained using an oil bath. In the reaction flask, 0.32 mol of toluene and 1.63 g of zeolite (activated at 438 K for 2 h) were introduced. The mixture was kept for heating and monochloroacetic acid (0.32 g) was also added (if required). The reaction mixture was stirred and heated to attain the reaction temperature (353 K) in the presence of nitrogen gas. The nitrogen gas was disconnected and chlorine gas was supplied at a rate of 0.04 mol/h. The chlorination was followed by the taking of samples of reaction mixture at suitable intervals. The analysis of the reaction mixture was done using a gas chromatograph (HP 5890 series II) with a flame ionization detector and a 50 m × 0.2 mm capillary column with methyl silicone gum. GC/MS and authentic samples were used for products identification.

The results of the chlorination of toluene with chlorine gas over different catalysts are presented in Table 2. The isomer distribution (PCT/OCT) obtained using a conventional catalyst, $FeCl_3$, is also included for comparison. In all experiments, the major products were *para*-chlorotoluene (PCT) and *ortho*-chlorotoluene (OCT). Small amounts of benzyl chloride (BC) and polychlorinated toluenes (others) were also detected. Metachlorotoluene isomer was found in trace quantity (<1%) in all cases. The products are found to be similar to those reported earlier for conventional catalysts (2).

Several zeolites were screened to get high *para/ortho* (*p/o*) selectivity. Different maximum yields of PCT and *p/o* ratios over various zeolites were obtained in the chlorination of toluene at similar levels of conversion and under the same conditions. The chlorination of toluene results first in *para*- and *ortho*-substituted products (parallel reaction) followed by a slow consecutive reaction to di-, tri-, and tetrachlorotoluenes. The selectivity for the parallel reaction is expressed as a *p/o* ratio. This ratio in parallel reaction is governed by the electrostatic forces

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TABLE 1

Physicochemical Properties of Zeolites

Zeolite	SiO_2/Al_2O_3 (molar ratio)	Cation composition (%)[a]		
		H^+	Na^+	K^+
K-ZSM-5	41	2.54	1.43	96.03
K-mordenite	22	7.50	2.75	89.75
K-X	2.38	—	7.39	92.60
K-Y	4.12	—	7.22	92.77
K-Beta	32.68	9.78	4.33	85.89
K-L	6.32	—	1.38	98.61
H K-L	6.32	75.61	0.95	23.44

[a] Values for Na^+ and K^+ were obtained by XRF analysis. H^+ was obtained by the difference between the Al content and the sum of the alkali metal values. Values are reported as percents of the total cation sites, taken as the aluminum content 100%.

produced in the zeolite channel by the cations and/or the restricted orientation of the adsorbed molecules and their transition states in the pores of the zeolite. However, the results obtained in the liquid phase chlorination of toluene over different zeolites cannot be taken as geometry related shape selectivity, Table 2 (10). The size, charge, position (potassium in this case), and electrostatic forces produced by cations in the zeolite channels may be responsible for the formation of *para*-chlorotoluene over K–L zeolite in the chlorination of toluene (3, 5). The results show a strong influence of different catalysts on the yields of PCT and *p*/*o* selectivity in the chlorination of toluene, which increase from 11.0 to 33.5% and 0.69 to 3.32%, respectively. The results are noteworthy and markedly higher compared to the $FeCl_3$ catalyst (Table 2). The highest *p*/*o* selectivity (3.32) was observed over K–L zeolite in the presence of monochloroacetic acid; however, *p*/*o* ratios over K–L (in the absence of $ClCH_2COOH$) and acidic H K–L zeolites were found to be 1.76 and 0.87, respectively. The role of monochloroacetic acid in enhancing the *para*-selectivity is not known yet. Similar *para*-selectivities were obtained in the chlorination of biphenyl over K–L + $ClCH_2COOH$, K–L, and H K–L zeolites (3). The maximum yield of benzyl chloride was obtained in the absence of catalyst, which may be attributed to the photochlorination of side chain of toluene (11). The catalysts, used in this study, could be arranged in the decreasing order of their *p*/*o* selectivity as follows:

K–L > K–L (no $ClCH_2COOH$) > H K–L ≈ K–Beta > K–Y > K–X ≈ K–mordenite ≈ K–ZSM-5 > $FeCl_3$ > None.

The ring (nuclear) and side chain chlorination of toluene take place by ionic and radical mechanisms, respectively, over zeolites (12). Electrophilic aromatic chlorination is feasible over Lewis and Brønsted acid catalysts. The Lewis and Brønsted acid sites polarize the chlorine molecule and produce the required positive chlorine by heterolytic dissociation which acts as an electrophile (11).

The influence of various solvents on the *p*/*o* selectivity was studied using zeolite K–L and monochloroacetic

TABLE 2

Chlorination of Toluene over Various Zeolites[a]

Catalyst	Unconverted toluene (wt%)	Yields (wt%)[b]				*p*/*o*[c] isomer ratio
		PCT	OCT	BC	Others	
K-ZSM-5	56.4	16.1	23.3	2.6	1.6	0.69
K-mordenite	57.3	15.2	21.9	3.9	1.7	0.69
K-X	60.0	11.0	16.0	11.1	1.9	0.69
K-Y	55.5	18.1	23.2	2.3	0.9	0.78
K-Beta	55.5	20.4	23.6	0.5	—	0.86
K-L	55.0	33.5	10.1	1.4	—	3.32
K-L[d]	54.7	27.1	15.4	2.1	0.7	1.76
H K-L	59.2	17.7	20.2	0.7	2.2	0.87
$FeCl_3$	55.9	11.7	23.9	5.6	2.9	0.49
None	51.5	0.5	1.2	45.0	1.8	0.42

[a] Reaction conditions: catalyst = 5 g/mol toluene; reaction temperature (K) = 353; $ClCH_2COOH$/catalyst (by weight) = 0.2; toluene = 0.32 mol; Cl_2 flow (mol/h) = 0.04.

[b] PCT, *para*-chlorotoluene; OCT, *ortho*-chlorotoluene; BC, benzylchloride; others, polychlorinated toluenes (di-, tri-, and tetrachlorotoluenes).

[c] *p*/*o* = PCT/OCT.

[d] Reaction in the absence of $ClCH_2COOH$.

TABLE 3

Solvent Effect in the Chlorination of Toluene over K–L Zeolite[a]

Solvent	Reaction temperature (C°)	Unconverted toluene (wt%)	Yields (wt%)[b]				p/o[c] isomer ratio
			PCT	OCT	BC	Others	
CH_2Cl_2	40	48.0	21.6	21.5	8.6	0.3	1.00
$ClCH_2CH_2Cl$	80	48.5	39.3	9.7	1.6	0.9	4.05
$ClCH_2CH_2Cl$	40	53.8	18.1	22.0	0.4	5.7	0.82
$CHCl_3$	55	59.0	17.1	18.6	3.8	1.5	0.92
$CHCl_3$	40	52.9	14.7	22.6	3.6	6.2	0.65
CCl_4	70	56.3	32.4	10.1	0.8	0.4	3.21
CCl_4	40	51.4	19.2	21.2	7.8	0.4	0.90
No solvent[d]	80	55.0	33.5	10.1	1.4	—	3.32
No solvent[d]	40	55.4	17.4	16.5	8.0	2.7	1.05

[a] Reaction conditions: catalyst = 10 g/mol toluene; $ClCH_2COOH$/catalyst (by weight) = 0.2; toluene = 0.16 mol; solvent = 15 ml; Cl_2flow (mol/h) = 0.04.

[b,c] See footnotes to Table 2.

[d] Reaction conditions are the same as those given in Table 2.

acid. The results of the solvent effect on the formation of more useful *p*-isomer are summarized in Table 3. The higher *p*/*o* (4.05) selectivity was obtained for the first time with the use of 1,2-dichloroethane as a solvent. The selectivity for *p*-isomer (*p*/*o* ratio) was found to be lower in the presence of other solvents (CH_2Cl_2, $CHCl_3$, CCl_4) compared to the values obtained even in the neat chlorination of toluene (Table 3). An increase in the reaction temperature increases the *p*/*o* ratio from 0.82 to 4.05 and the maximum yield of PCT from 18.1 to 39.3% when 1,2-dichloroethane is used as solvent (Table 3). Robertson *et al.* (*13*) and Andrews *et al.* (*14*) reported that the reaction temperature influences overall halogen order and thus, the activation energy for reactions which differ with the change in molecularity in halogen is not necessarily the same. These factors may be influencing *p*/*o* selectivity as reaction temperature increases. In the case of chlorination of biphenyl (3) and benzene (4) over K–L zeolite, it was observed earlier that dichloromethane and 1,2-dichloroethane gave very high *para*-selectivity for 4,4′-dichlorobiphenyl and 1,4-dichlorobenzene, respectively. These authors suggested that the use of some solvents may influence the activation of reactants or diffusion and transport process in the zeolite channels. In addition, Olah *et al.* (15) reported that the increasing dielectric constant of the solvents increases the rupture of the bond between the two atoms of the chlorine molecule, which facilitates the reaction. In particular, 1,2-dichloroethane may be acting in a similar way in the chlorination of toluene compared to the other solvents.

It can be concluded from the data presented in this paper that zeolite K–L in the presence of monochloroacetic acid acts as a *para*-selective catalyst for the chlorination of toluene. The solvent (1,2 dichloroethane) was found to enhance the yield of *para*-chlorotoluene. The higher *p*/*o* selectivity is obtained by raising the reaction temperature.

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REFERENCES

1. Olah, G. A., "Friedel Crafts Chemistry," p. 509. Wiley, New York, 1973.
2. Kamigata, N., Satoh, T., Yoshida, M., Matsuyama, H., and Kameyama, M., *Bull. Chem. Soc. Jpn.* **61,** 2226 (1988).
3. Botta, A., Buysch, H. J., and Puppe, L., *Angew. Chem. Int. Ed. Engl.* **30,** 1689 (1991).
4. Nakamura, T., Shihoda, K., and Yasuda, K., *Chem. Lett.*, 1881 (1992).
5. Wortel, Th. M., Oudijn, D., Vleugel, C. J., Roelofsen, D. P., and van Bekkum, H., *J. Catal.* **60,** 110 (1979).
6. Suzuki, T., and Komatsu, C., U.S. Patent 4 831 199 (1989).
7. Ratnasamy, P., Singh, A. P., and Joshi, P. N., Indian Patent 926/DEL/1992.
8. Argauer, R. J., and Landolt, G. R., U.S. Patent 3,702,886 (1972).
9. Camblor, M. A., and Péréz Pariente, J., *Zeolites* **11,** 202 (1991).

10. Csicsery, S. M., *Pure Appl. Chem.* **58,** 841 (1986).
11. Delaude, L., and Laszlo, P., *J. Org. Chem.* **55,** 5260 (1990).
12. Braendlin, H. P., and McBee, E. T., *in* "Friedel Crafts and Related Reactions" (G. A. Olah, Ed.), Vol. 3, p. 1517. Wiley–Interscience, New York, 1964.
13. Robertson, P. W., de la Mare, P. B. D., and Johnston, W. T. G., *J. Chem. Soc.* 276 (1943).
14. Andrews, J. L., and Keefer, R. M., *J. Am. Chem. Soc.* **79,** 5169 (1957).
15. Olah, G. A., Kuhn, S. J., and Hardie, B. A., *J. Am. Chem. Soc.* **86,** 1055 (1964).

A. P. Singh[1]
Sujit B. Kumar
A. Paul
Anuj Raj

Catalysis Division
National Chemical Laboratory
Pune 411 008, India

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[1] To whom correspondence should be addressed.