Selective chlorination of 4-chlorotoluene to 2,4-dichlorotoluene over zeolite catalysts

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The performance of various zeolites in the liquid phase chlorination of 4-chlorotoluene (4-CT) with gaseous chlorine at a moderate temperature and normal pressure has been examined. A comparison under the same conditions with Lewis acid catalyst $FeCl_3$, is also carried out. It is found that zeolite K-L exhibits higher selectivity for 2,4-dichlorotoluene (2,4-DCT/3,4-DCT = 3.54) compared to the other zeolites studied and also $FeCl_3$ catalyst (2,4-DCT/3,4-DCT = 3.18), while the rate of 4-CT conversion (75.8 mmol g^{-1} h^{-1}) is found to be comparable on K-L and $FeCl_3$ catalysts. The highest rate of 4-CT conversion, among the catalysts studied is obtained over K-beta (101.4 mmol g^{-1} h^{-1}). $FeCl_3$ catalyst produces higher amounts of tri- and tetra-substituted products due to its non-shape-selective character. Mainly the side-chain chlorinated product (α,4-dichlorotoluene) is obtained over K-X, amorphous SiO_2 and in the absence of catalyst. Solvents influence the rate of 4-CT conversion as well as the 2,4-DCT/3,4-DCT isomer ratio. 1,2-dichloroethane appears to be the best solvent in enhancing the 2,4-DCT/3,4-DCT isomer ratio when the reaction temperature is raised from 313 to 353 K.

Keywords: chlorination of 4-chlorotoluene; preparation of 2,4-dichlorotoluene; zeolite K-L

1. Introduction

2,4-dichlorotoluene (2,4-DCT) is used via its side-chain chlorinated intermediate to produce fungicides, dyes, pharmaceuticals, preservatives and peroxides (curing agents for silicones and polyesters) etc. [1]. Industrially, 2,4-DCT is obtained by the reaction of liquid 4-CT with gaseous chlorine in the presence of Lewis acid catalysts such as $SbCl_3$ [2], $ZrCl_4$ [3] and $FeCl_3$ [3]. 2,4-DCT is also formed up to 60% yield by the chlorination of 4-CT catalysed by metal sulphides or metal halide–sulphur compound co-catalyst systems [3]. In another method, ring chlorination of 2-chlorotoluene yields a mixture of all four possible dichlorotoluenes, the 2,3-, 2,4-, 2,5- and 2,6-isomers. The major isomer, 2,5-dichlorotoluene, constitutes up to 60% of the product mixture [3,4]. The Lewis acid catalysts have several disadvantages if applied to industrial processes: wasting large amounts of catalysts, corrosion of reactors, water pollution by acidic waste water, difficulty of catalyst recovery and formation of large amounts of consecutive products. Zeolites are known for their shape-selective and catalytic behaviour in the field of petrochemistry [5,6] and organic transformations [7]. However, little is known about their efficiency in the halogenation of aromatics [8–13]. Recently, zeolites have been used by us in the selective chlorination of aromatics [14–18]; however, their properties had not been exploited so far in the selective chlorination of 4-CT to 2,4-DCT. The objective of the present study is to enhance the yield of 2,4-DCT and to minimize the formation of consecutive (tri- and tetrachlorotoluenes) and side-chain products (α,4-DCT) in the chlorination of 4-CT using zeolite catalysts.

This paper presents the results of a study comparing the performance of various catalysts in the chlorination of 4-chlorotoluene. The influence of various solvents on the product yields and the rate of 4-CT conversion is also reported.

2. Experimental

Zeolite beta, K-L and ZSM-5 were synthesized following the procedure described in the literature [19–21]. Samples of beta and ZSM-5 were activated after synthesis. They were calcined at 773 K for 16 h in dry air. These samples were then converted into their potassium form by ion-exchange with 1 M KNO_3 solution (5 g zeolite; 50 ml 1 M KNO_3; temperature 353 K; three exchanges). Na-X and Na-Y were obtained from Laporte Inorganics, Cheshire, UK. Their K-form was obtained following the procedure mentioned above.

The chemical composition of the catalysts was determined by atomic absorption analysis after dissolution of the sample (Hitachi 800). All the samples were examined by X-ray diffraction (Rigaku, D-max/III-VC model) using Cu Kα radiation. The size and morphology of the catalysts were determined by scanning electron microscopy. The surface area of the catalysts was measured by the nitrogen BET method. The properties of the catalysts are listed in table 1.

Reactions were performed in the liquid phase under

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Table 1
Physico-chemical properties of zeolites

Zeolite	SiO_2/Al_2O_3 (molar ratio)	Cation composition (%) [a]			Surface area [b] (m^2/g)	Crystal size (μm)
		H^+-	Na^+-	K^+-		
K-ZSM-5	41.0	2.5	1.4	96.1	410	0.5
K-mordenite	22.0	7.5	2.7	89.8	542	1.0
K-beta	26.0	9.8	4.3	85.9	743	0.5
K-X	2.4	–	7.4	92.6	615	1.0
K-Y	4.1	–	7.2	92.8	606	1.0
K-L	6.8	–	1.4	98.6	215	0.2

[a] Na^+- and K^+-ions were analysed by XRF. H^+ was obtained by the difference between the Al content and the sum of the alkali metal values. Values are reported as percent of the total number of cation sites with aluminum content taken as 100%.

[b] N_2 adsorption.

batch conditions. The corresponding catalyst (0.75 g) (activated at 433 K for 2 h) was added to 4-CT (0.2 mol) and the resulting suspension was magnetically stirred for 30 min in the presence of nitrogen at the corresponding temperature (368 K) maintained using an oil bath. The nitrogen gas was disconnected and chlorine gas was supplied at the rate of 0.09 mol/h to conduct the reaction. The course of the reaction was periodically followed by analyzing the reaction mixture using a Blue Star model 421 gas-chromatograph equipped with FID detector and 50 m × 0.2 mm capillary column with methyl silicone gum. The products were identified using gas chromatography–mass spectrometry (GC-MS) and authentic samples.

3. Results and discussion

3.1. *Various catalysts*

The catalytic activity and selectivity (2,4-DCT/3,4-DCT isomer ratio) obtained with different zeolite catalysts, under similar reaction conditions, are given in table 2. The results with amorphous silica, $FeCl_3$ and in the absence of catalyst (uncatalyzed reaction) are also included for comparison. The reaction produces a mixture of 2,4-DCT and 3,4-DCT as major products, α,4-dichlorotoluene (α,4-DCT) and others (tri- and tetrachlorotoluenes) are also formed with almost all catalysts. However, the concentrations of α,4-DCT and others, in the reaction mixture, depend upon the type of catalyst and the reaction conditions. The formation of 2,4-DCT and 3,4-DCT results from the aromatic substitution of 4-CT by parallel reactions while tri- and tetrachlorotoluenes are obtained by the consecutive reactions of 2,4-DCT and 3,4-DCT [12,15].

As can be seen from table 2, zeolite K-L exhibits the best selectivity (2,4-DCT/3,4-DCT = 3.54) in this study, although, the activity (rate of 4-CT conversion) over K-L zeolite is somewhat lower (75.8 mmol g^{-1} h^{-1}) than H-beta (101.4 mmol g^{-1} h^{-1}) (table 2). Other zeolite catalysts studied in this reaction are practically less active and selective than K-L (table 2). Zeolite K-L and $FeCl_3$ catalysts show comparable activities (75.8 mmol g^{-1} h^{-1}), but $FeCl_3$ is found to be less selective (2,4-DCT/3,4-DCT = 3.18) than K-L. In addition, yields of secondary consecutive products increase by a factor of 7.4 over $FeCl_3$ compared to K-L. In the absence of catalyst, only side-chain chlorinated product (α,4-DCT) is obtained which may be attributed to the photochlorina-

Table 2
Chlorination of 4-chlorotoluene [a]

Catalyst	Activity [b] (mmol g^{-1} h^{-1})	Unconverted PCT (wt%)	Product yields (wt%) [c]				2,4-/3,4-isomer ratio
			2,4-DCT	3,4-DCT	α,4-DCT	others	
none	–	92.4	–	–	7.6	–	–
SiO_2 [d]	56.1	57.4	10.0	3.3	26.9	2.4	3.03
$FeCl_3$	75.8	42.7	33.4	10.5	–	13.4	3.18
K-ZSM-5	46.6	64.8	18.1	8.0	8.3	0.8	2.26
K-mordenite	27.9	78.9	8.3	3.0	9.0	0.8	2.77
K-beta	101.4	23.3	49.5	25.1	0.1	2.0	1.97
K-X	47.5	64.1	1.6	0.7	31.7	1.9	2.28
K-Y	50.9	61.5	13.1	6.2	16.8	2.4	2.11
K-L	75.8	42.7	41.8	11.8	1.9	1.8	3.54

[a] Reaction conditions: catalyst = 3.78 g/mol PCT; reaction temperature = 368 K; PCT = 0.2 mol; Cl_2 flow = 0.09 mol/h; reaction time = 2 h.

[b] Activity = PCT(para-chlorotoluene) conversion rate (mmol g^{-1} h^{-1}) = mass of 4-CT converted / (mass of catalyst used × reaction time in h).

[c] 2,4-DCT = 2,4-dichlorotoluene; 3,4-DCT = 3,4-dichlorotoluene, α,4-DCT = α,4-dichlorotoluene, others = tri- and tetra-chlorotoluenes.

[d] Fumed silica type S-5005 supplied by Sigma Chemical, MO, USA.

tion of the $-CH_3$ group of 4-CT [22,23]. Even amorphous SiO_2 is not able to enhance the yield of ring-chlorinated products, which indicates that K-L acts as a selective catalyst in increasing the yields of substituted products and consequently the ratio of 2,4-DCT/3,4-DCT. The formation of a small amount of α,4-DCT even in the presence of catalyst may be related to insufficient darkness which may initiate the free radical reactions.

The activity at 368 K is in the decreasing order:

$$\text{K-beta} > \text{K-L} \approx FeCl_3 > SiO_2 > \text{K-Y} > \text{K-X}$$
$$> \text{K-ZSM-5} > \text{K-mordenite} > \text{none}.$$

The selectivity (2,4-DCT/3,4-DCT ratio) of different catalysts (table 2) decreases in the order:

$$\text{K-L} > FeCl_3 > SiO_2 > \text{K-mordenite} > \text{K-X}$$
$$\approx \text{K-ZSM-5} > \text{K-Y} > \text{K-beta}.$$

The results confirm that zeolite K-L enhances the selectivity for 2,4-DCT and that the para-selectivity in the chlorination reactions cannot be interpreted alone in terms of geometry related shape-selectivity. Zeolites of similar pore diameter but of different types behave in different ways. Previous studies show that the type of zeolite, charge, position and spatial arrangement of the cations and their force fields in the zeolites are responsible for the activation of chlorine molecules and selective formation of para-products [12,24]. In another study, it is reported that selective para-substitution of aromatics in the chlorination reactions takes place by a specific orientation of the aromatic in the cavities of the zeolite. The steric hindrance at the ortho-position is caused by the walls of the cavities while the para-position is activated by electrostatic influences [11]. Presumably, the above-mentioned factors may account for the activation of the Cl_2 molecule and selective formation of 2,4-DCT in the chlorination of 4-CT using zeolite K-L.

3.2. Solvent effect

As the reaction is carried out in the liquid phase, the catalyst performance is greatly influenced by the nature of the solvent. Usually, the solvent affects both the isomer ratio and the rate of 4-CT conversion. Some results on the rate of 4-CT conversion and on the 2,4-DCT/3,4-DCT isomer ratio for the chlorination of 4-CT over zeolite K-L in dichloromethane, 1,2-dichloroethane, chloroform, carbon tetrachloride and in the absence of solvent are presented in this paper (table 3). Product yields are observed to be dependent on the reaction solvent. Dichloromethane and 1,2-dichloroethane appear to be the best solvents and the isomer ratio 2,4-DCT/3,4-DCT is found to be 4.10 and 3.61 respectively, at 313 K. The other solvents are not found to be effective enough to give higher isomer ratio than the values obtained even in the neat chlorination of 4-CT (3.54). More satisfactory reaction rates are obtained by raising the reaction temperature, which has no significant effect on the 2,4-DCT/3,4-DCT ratio except in the case of 1,2-dichloroethane. As the temperature is increased from 313 to 353 K in the presence of 1,2-dichloroethane, the rate of 4-CT conversion increases from 9.4 to 28.4 mmol g^{-1} h^{-1} and the ratio of 2,4-DCT/3,4-DCT increases from 3.62 to 4.34 respectively. The corresponding yield of 2,4-DCT also increases from 13.4 to 43.9 wt% respectively. The 2,4-DCT/3,4-DCT isomer ratio in different solvents at 313 K is found to be in the order:

$$CH_2Cl_2 > ClCH_2CH_2Cl > CHCl_3 \approx CCl_4.$$

The rate of 4-CT conversion in different solvents at 313 K is found to be in the order:

$$CCl_4 > CH_2Cl_2 > CHCl_3 > ClCH_2CH_2Cl.$$

It has been reported earlier [24] that in the chlorination reactions solvents do not act only as a diluent. Botta

Table 3
Influence of solvent in the chlorination of PCT [a]

Solvent	Reaction temp. (K)	PCT conv. rate [b] (mmol g^{-1} h^{-1})	Unconverted PCT (wt%)	Product yields (wt%) [c]				2,4-/3,4-isomer ratio
				2,4-DCT	3,4-DCT	α,4-DCT	others	
CH_2Cl_2	313	19.8	59.9	27.1	6.6	3.9	2.5	4.10
$ClCH_2CH_2Cl$	353	28.4	42.8	43.9	10.1	2.1	1.1	4.34
$ClCH_2CH_2Cl$	313	9.4	81.0	13.4	3.7	1.1	0.8	3.62
$CHCl_3$	333	18.7	62.4	24.2	6.8	4.5	2.1	3.56
$CHCl_3$	313	12.5	74.8	12.8	3.6	7.7	1.1	3.55
CCl_4	348	46.0	7.2	61.6	17.6	3.2	10.4	3.50
CCl_4	313	23.7	52.2	30.5	8.6	5.3	3.4	3.54
none [d]	368	75.8	42.7	41.8	11.8	1.9	1.8	3.54
none [d]	313	64.3	48.6	37.9	10.7	1.3	1.5	3.54

[a] Reaction conditions: catalyst = 10.1 g/mol PCT; PCT = 0.1 mol; solvent = 12.5 g; Cl_2 flow = 0.09 mol/h. Reaction time = 2 h.
[b,c] See footnotes to table 2.
[d] Reaction conditions the same as in table 2.

et al. [24] have reported that dichloromethane gives very high selectivity for 4,4′-dichlorobiphenyl in the chlorination of biphenyl in the presence of zeolite K-L. In another study, Nakamura et al. [25] observed that 1,2-dichloroethane favours the formation of 1,4-dichlorobenzene in the chlorination of benzene using K-L. These authors suggest that these solvents may influence the activation of the reactants, diffusion and transport process in the zeolite channels. In our study, dichloromethane and 1,2-dichloroethane may be influencing the product ratio in a similar way.

4. Conclusions

Zeolite K-L catalyzes the chlorination of 4-chlorotoluene selectively to 2,4-dichlorotoluene with gaseous chlorine and is superior to various other zeolite catalysts and $FeCl_3$. 1,2-dichloroethane gives the highest selectivity at 353 K. The rate of 4-CT conversion and ratio of 2,4-DCT/3,4-DCT increase with the increase in reaction temperature in the presence of 1,2-dichloroethane.

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