

# Selective chlorination of 4-chlorotoluene using zeolite catalysts

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## Abstract

The synthesis of 2,4-dichlorotoluene (2,4-DCT) has been investigated at 368 K and at atmospheric pressure using a series of zeolite catalysts and also the conventional catalyst,  $\text{FeCl}_3$ , in the liquid phase chlorination of 4-chlorotoluene (4-CT) with gaseous chlorine ( $\text{Cl}_2$  flow = 0.09 mol/h) and catalyst concentration of 3.78 g/mol 4-CT. Zeolite K-L catalyzes 4-CT selectively to 2,4-DCT and is superior to the other zeolites and  $\text{FeCl}_3$  in terms of selectivity. The highest rate of 4-CT conversion ( $96.4 \text{ mmol g}^{-1} \text{ h}^{-1}$ ) is achieved over acidic H(26.1)K-L, and the rate of 4-CT conversion over zeolite K-L and  $\text{FeCl}_3$  is 75.6 and  $79.6 \text{ mmol g}^{-1} \text{ h}^{-1}$ , respectively. But the  $\text{FeCl}_3$  catalyst produces higher amounts of consecutive reaction products compared to K-L. Zeolite K-X, amorphous  $\text{SiO}_2$  and the uncatalysed reaction preferably give the side-chain chlorinated product ( $\alpha$ ,4-dichlorotoluene). The activity and selectivity (ratio of 2,4-DCT/3,4-DCT) of zeolite K-L depend on the reaction conditions and on the solvent used in the reaction. Solvents influence the rate of 4-CT conversion and the isomer ratio of 2,4-DCT/3,4-DCT. 1,2-dichloroethane is a suitable solvent in this reaction and the highest yield of 2,4-DCT (43.9 wt% at 57.2 wt% conv. of 4-CT) and isomer ratio (2,4-DCT/3,4-DCT = 4.3) are achieved in 1,2-dichloroethane at 353 K. On increasing the reaction time, the amount of zeolite K-L and the reaction temperature, the yield of 2,4-DCT increases. However, the change in isomer ratio (2,4-DCT/3,4-DCT) is negligible. Partial cation exchange in zeolite K-L decreases the rate of 4-CT conversion in the order: H(26.1)K-L > Li(12.1)K-L > Na(9.8)K-L > Cs(21.7)K-L > La(3.7)K-L > K-L. In terms of activity, HCl treated zeolite K-L is less active than parent K-L. Also, zeolite K-L is a recyclable and regenerable catalyst. The slight increase in  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, degree of  $\text{K}^+$  exchange and crystallinity of K-L may be attributed to the production of HCl during the reaction. The reaction appears to proceed by an electrophile ( $\text{Cl}^+$ ), followed by the interaction of  $\text{Cl}^+$  with 4-CT, resulting in the desired product. © 1997 Elsevier Science B.V.

**Keywords:** 4-chlorotoluene; 2,4-dichlorotoluene; Zeolite K-L

## 1. Introduction

2,4-Dichlorotoluene is a very important intermediate which is used in the manufacture of fungicide, dyes, pharmaceuticals, preservatives, and peroxides (curing agents for silicones and polyesters) [1]. In the industrial plant, 2,4-DCT is obtained by the reaction of liquid 4-CT with

gaseous chlorine in the presence of Lewis acid catalysts such as  $\text{SbCl}_3$  [2],  $\text{ZrCl}_4$  [3] and  $\text{FeCl}_3$  [3]. 2,4-DCT is also produced up to 60% yield by the chlorination of 4-CT catalyzed by metal sulphides or metal halide-sulphur compound co-catalyst system [3]. In another method, ring chlorination of 2-chlorotoluene yields a mixture of all four possible chlorotoluenes, the 2,3-, 2,4-, 2,5-, and 2,6-isomers. The major isomer, 2,5-dichlorotoluene, constitutes 60% of the

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product mixture [3,4]. 2,4-DCT can also be produced by the isomerization of dichlorotoluenes [5,6]. Thus, the resulting isomers can be separated by using the medium pore molecular sieve,  $\text{AlPO}_4\text{-11}$  [7]. The Lewis acid catalysts have several disadvantages if applied to industrial process; wasting large amounts of catalyst, 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 the shape-selective and catalytic behaviour in the field of petrochemistry [8,9] and organic transformations [10]. However, little is known about their efficiency in the halogenation of aromatics [11–16]. Very recently, zeolites have been used by us in the selective chlorination of aromatics [17–21], however, their properties have not been exploited so far in the selective chlorination of 4-chlorotoluene to 2,4-dichlorotoluene except for a preliminary report [22]. The aim of the present study is to enhance the yield of 2,4-DCT and to minimize the formation of consecutive (tri- and tetra-chlorotoluenes) and side-chain ( $\alpha$ ,4-dichlorotoluene) products in the chlorination of 4-CT using zeolite catalysts.

In this work, various catalysts are investigated in order to evaluate the influence of different zeolite structures on the formation of 2,4-DCT. Their catalytic behaviour has been compared with that of the conventional catalyst  $\text{FeCl}_3$ , and amorphous  $\text{SiO}_2$ . The present study also focuses on the effect of reaction time, various solvents, partial exchange of cations in KL, catalyst concentration, reaction temperature, zeolite KL treated with HCl and reuse of zeolite KL on the rate of 4-CT conversion, isomer ratio of 2,4-DCT/3,4-DCT and product yields in the chlorination of 4-chlorotoluene.

## 2. Experimental

Zeolite beta, K-L and ZSM-5 are prepared by hydrothermal methods, according to the procedures reported in the literature [23–25]. All

synthesized zeolites are calcined at 773 K for 16 h in dry air. These samples (5 g each) are then converted into their potassium forms by ion-exchange with 1 M  $\text{KNO}_3$  solution (50 ml) at 353 K by repeated exchanges (minimum three times exchange). The H(26.1)K-L is prepared by a conventional ion-exchange method in which 5 g of the parent K-L is treated with 50 ml of 0.1 M aqueous solution of  $\text{NH}_4\text{NO}_3$  at room temperature for 24 h. The resulting  $\text{NH}_4\text{-KL}$  sample is separated by filtration, washed with deionised water, dried at 373 K and calcined at 773 K for 12 h. The Li(12.1)K-L, Na(9.8)K-L and Cs(21.1)K-L zeolites are prepared by conventional ion-exchange methods in which the zeolite K-L is treated once with their corresponding 0.1 M chloride solutions at room temperature. La(3.7)K-L is prepared by solid state ion-exchange of K-L with  $\text{La}(\text{NO}_3)_3$ . The zeolite K-L is mixed with 5 wt% of  $\text{La}(\text{NO}_3)_3$  and heated at 773 K for 24 h. The La(3.7)K-L thus obtained is washed with deionized water and dried at 373 K. Other zeolites, Na-X and Na-Y, are obtained commercially from Laporte Inorganics, Cheshire, UK. These zeolites are converted into their K-forms following the above mentioned procedure. Various HCl treated zeolite K-L samples are prepared by mixing parent K-L with different molar solutions of HCl (0.05 to 0.7 M HCl) at a ratio of 5 g zeolite/50 ml of HCl solution for 24 h at room temperature. Further, the resulting zeolites are exchanged with 1 M  $\text{KNO}_3$  solution to ensure > 98% K-exchange in each sample.

The cationic contents and silica to alumina ratio of these catalysts are determined by wet chemical and atomic absorption spectrometer (Hitachi Z-800) after dissolution of the sample. X-ray diffraction (XRD) patterns of zeolites are obtained with  $\text{Cu K}\alpha$  radiation (Rigaku, D-max/III-VC model). The crystal size of the zeolites is determined by scanning electron microscopy (Shimadzu model UV-2101 PC). The  $\text{N}_2$  BET surface areas of all the zeolites are measured with a surface area analyzer (Omni-sorb 100 CX apparatus). Prior to use, the cata-

lyst is activated at 433 K for 2 h. The properties of all the zeolites are reported in Table 1.

The chlorination of 4-CT is carried out batch-wise in a 100 ml glass reactor with continuous stirring. In a typical run, the corresponding activated catalyst (0.75 g) is added to 4-CT (0.2 mol) and the resulting suspension is magnetically stirred for 30 min in the presence of nitrogen (20 ml/min) at 368 K which is maintained using an oil bath. Then nitrogen gas is disconnected and chlorine gas is supplied at a rate of 0.09 mol/h to conduct the reaction. The course of the reaction is periodically followed by analyzing the reaction mixture using a Blue Star model 421 gas-chromatograph equipped with FID detector and 50 m  $\times$  0.2 mm capillary column with methyl silicone gum. The products are identified using gas-chromatography–mass spectrometry and the authentic samples.

The rate of 4-CT conversion ( $\text{mmol g}^{-1} \text{h}^{-1}$ ), conversion of 4-CT (wt%) and product yields (wt%) are defined as follows:

Rate of 4-CT conversion ( $\text{mmol g}^{-1} \text{h}^{-1}$ )

$$= (\text{mass of 4-CT converted}) / (\text{mass of catalyst used} \times \text{reaction time}) \text{h}^{-1},$$

Conversion of 4-CT (wt%)

$$= (\text{amount of 4-CT reacted}) / (\text{amount of 4-CT fed}) \times 100,$$

Product yield (wt%)

$$= (\text{amount of 4-CT converted}) \times (\text{selectivity of a particular product} \in \text{the products}) / 100.$$

### 3. Results and discussion

The chemical composition and properties of the zeolites used in the present study are given in Table 1. X-ray diffraction studies indicate high crystallinity and absence of any other phases in all samples. XRD examination also give no evidence of structure change of the zeolite K-L after various cation-exchange and HCl treatments, however, the crystallinity of the zeolite K-L samples decreases with the HCl treatment (0.3 to 0.7 M HCl solutions). The surface area and scanning electron micrographs reveal well defined materials without any occluded material in the zeolites.

#### 3.1. Effect of various catalysts

The conversion of 4-CT (wt%), initial rate of 4-CT conversion ( $\text{mmol g}^{-1} \text{h}^{-1}$ ), product yields (wt%) and isomer ratio of 2,4-DCT/3,4-DCT obtained over various zeolite catalysts are listed in Table 2. The results with amorphous silica,  $\text{FeCl}_3$  and in the absence of any catalyst

Table 1  
Physico-chemical properties of zeolites

Zeolite	$\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio)	Cation composition (%) <sup>a</sup>			Surface area <sup>b</sup> ( $\text{m}^2/\text{g}$ )	Crystal size ( $\mu\text{m}$ )
		$\text{H}^+$	$\text{Na}^+$	$\text{K}^+$		
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
H(26.1)K-L <sup>c</sup>	6.8	26.1	—	73.9	221	0.5

<sup>a</sup>  $\text{Na}^+$  and  $\text{K}^+$ -ions were analysed by XRF.  $\text{H}^+$  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 cation sites with aluminum content taken as 100%.

<sup>b</sup>  $\text{N}_2$  adsorption.

<sup>c</sup> Value in parentheses represent the percentage of  $\text{H}^+$  in K-L.

are also included for the comparison. The reaction produces a mixture of 2,4-DCT and 3,4-dichlorotoluene (3,4-DCT) as major products.  $\alpha$ ,4-dichlorotoluene ( $\alpha$ ,4-DCT) and others (tri- and tetra-chlorotoluenes) are also formed with almost all catalysts. However, the concentration of  $\alpha$ ,4-DCT and others, in the reaction mixture, depend upon the type of the 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 tetra-chlorotoluenes are obtained by the consecutive reactions of 2,4-DCT and 3,4-DCT [15,18].

As can be seen from the results of 1 h (Table 2), zeolite K-L exhibits the best selectivity (2,4-DCT/3,4-DCT = 3.4) in this study, although, the activity (initial rate of 4-CT conversion) over zeolite K-L is somewhat lower (75.6 mmol

$\text{g}^{-1} \text{h}^{-1}$ ) than H(26.1)K-L (96.4 mmol  $\text{g}^{-1} \text{h}^{-1}$ ) and K-beta (93.3 mmol  $\text{g}^{-1} \text{h}^{-1}$ ). The higher rate of 4-CT conversion over acidic H(26.1) K-L compared to the basic K-L may be attributed to its acidic nature [26]. Zeolite K-L is found to be slightly less active (75.6 mmol  $\text{g}^{-1} \text{h}^{-1}$ ) than  $\text{FeCl}_3$  (79.6 mmol  $\text{g}^{-1} \text{h}^{-1}$ ). However, consecutive products increase by a factor of 7.4 over  $\text{FeCl}_3$  compared to K-L after 2 h of reaction time. In the absence of catalyst, only side-chain chlorinated product ( $\alpha$ ,4-DCT) is obtained which may be attributed to the photochlorination of  $-\text{CH}_3$  group of 4-CT [26,27]. Even amorphous  $\text{SiO}_2$  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.

Table 2  
Chlorination of 4-chlorotoluene <sup>a</sup>

Catalyst	Reaction time (h)	Conv. of 4-CT (wt%)	Initial <sup>b</sup> rate of 4-CT conv. (mmol $\text{g}^{-1} \text{h}^{-1}$ )	Product yields (wt%) <sup>c</sup>				2,4-/3,4- <sup>d</sup> isomer ratio
				2,4-DCT	3,4-DCT	$\alpha$ ,4-DCT	others	
None	1	4.8	—	—	—	4.8	—	—
	2	7.6	—	—	—	7.6	—	—
$\text{SiO}_2$ <sup>e</sup>	1	19.5	51.4	9.0	3.0	7.2	0.3	3.0
	2	42.6	—	10.0	3.3	26.9	2.4	3.0
$\text{FeCl}_3$	1	30.2	79.6	19.5	6.3	—	4.4	3.1
	2	57.3	—	33.4	10.5	—	13.4	3.2
K-L	1	28.7	75.6	21.5	6.3	0.3	0.6	3.4
	2	57.3	—	41.8	11.8	1.9	1.8	3.5
H(26.1)K-L <sup>f</sup>	1	36.6	96.4	26.5	8.5	0.5	1.1	3.1
	2	73.1	—	49.2	14.7	2.9	6.3	3.3
K-beta	1	35.4	93.3	23.8	11.5	—	0.1	2.1
	2	76.7	—	49.5	25.1	0.1	2.0	2.0
K-mordenite	1	9.2	24.2	5.5	2.0	1.4	0.3	2.8
	2	21.1	—	8.3	3.0	9.0	0.8	2.8
K-Y	1	17.0	44.8	8.1	3.8	4.6	0.5	2.1
	2	38.5	—	13.1	6.2	16.8	2.4	2.1
K-X	1	15.6	41.1	0.8	0.3	14.2	0.3	2.7
	2	35.9	—	1.6	0.7	31.7	1.9	2.3
K-ZSM-5	1	18.3	48.2	10.2	4.8	3.1	0.2	2.1
	2	35.2	—	18.1	8.0	8.3	0.8	2.3

<sup>a</sup> Reaction conditions: Catalyst = 3.78 g/mol 4-CT; 4-CT = 0.2 mol; reaction temperature = 368 K;  $\text{Cl}_2$  flow = 0.09 mol/h.

<sup>b</sup> Initial rate of 4-CT conversion (mmol  $\text{g}^{-1} \text{h}^{-1}$ ) is defined as mass of 4-CT converted/(mass of catalyst used)  $\times$  (reaction time)  $\text{h}^{-1}$ .

<sup>c</sup> 2,4-DCT = 2,4-dichlorotoluene; 3,4-DCT = 3,4-dichlorotoluene;  $\alpha$ ,4-DCT =  $\alpha$ ,4-dichlorotoluene; others = tri- and tetra-chlorotoluenes.

<sup>d</sup> Isomer ratio of 2,4-DCT/3,4-DCT.

<sup>e</sup> Fumed silica type S-5005 supplied by Sigma Chemical, MO, USA.

<sup>f</sup> Value in parentheses correspond to the percentage of  $\text{H}^+$  in K-L.

The activity of various catalysts at 368 K after 1 h of reaction time is found to be in the decreasing order: H(26.1)K-L > K- $\beta$  > FeCl<sub>3</sub> > K-L > SiO<sub>2</sub> > K-ZSM-5 > K-Y > K-X > K-mordenite.

The isomer ratio (2,4-DCT/3,4-DCT) after 1 h of reaction time over different catalysts decreases in the order: K-L > H(26.1)K-L  $\cong$  FeCl<sub>3</sub> > SiO<sub>2</sub> > K-mordenite > K-X > K-ZSM-5 > K-Y > K- $\beta$ .

The results of Table 2 confirm that conventional concept of geometry-related shape selectivity alone cannot be taken to explain the variations in the para-selectivity in the chlorination of aromatics over zeolite catalysts [11,28]. Zeolites of similar pore diameter but of different structural types behave in different ways. It is reported [28] that the factors that actually direct the substitution are the ionic radius, charge and spatial arrangement of the exchanged cations and their force fields. Presumably, the above mentioned factors may be accounted for the activation of Cl<sub>2</sub> molecule and selective formation of 2,4-DCT in the chlorination of 4-CT using zeolite K-L.

The reaction appears to proceed by an electrophile (Cl<sup>+</sup>) which is produced by heterolytic dissociation of Cl<sub>2</sub> molecule over catalysts followed by interaction of Cl<sup>+</sup> with 4-CT, resulting in the formation of ring chlorinated products [18,26,29,30]. The side-chain chlorination of -CH<sub>3</sub> group of 4-CT takes place by radical mechanism [26,27].

### 3.2. Duration of the run using various catalysts

The relationship between conversion and reaction time for 4-CT chlorination over various catalysts is illustrated in Fig. 1. In all experiments a temperature of 368 K and 3.78 g catalyst/mol of 4-CT are used. As seen in Fig. 1, the conversion of 4-CT increases gradually over all catalysts with the progress of the reaction. The highest and comparable conversions of 4-CT are maintained over H(26.1)K-L and K-beta zeolites in the investigated range of reaction time. Further, the conversion of 4-CT over

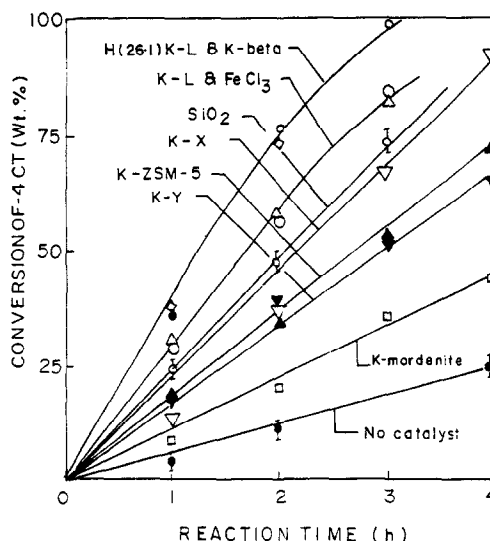


Fig. 1. Conversion of 4-CT over various catalysts as a function of reaction time (h). Reaction conditions: catalyst (g/mol 4-CT) = 3.78; Reaction temperature (K) = 368; 4-CT (mol) = 0.2; Cl<sub>2</sub> flow (mol/h) = 0.09.

zeolite K-L is found to be almost identical to that over the Lewis acid catalyst, FeCl<sub>3</sub>. Zeolites K-mordenite, K-Y, and K-ZSM-5 exhibit comparatively lower activities in the chlorination of 4-CT.

### 3.3. 2,4-DCT/3,4-DCT isomer ratio versus 4-CT conversion

In order to compare the selectivity (2,4-DCT/3,4-DCT) of examined catalysts, the isomer ratio of 2,4-DCT/3,4-DCT is plotted as a function of conversion of 4-CT in Fig. 2. As shown in this figure, the ratio of 2,4-DCT/3,4-DCT over zeolite K-L is higher throughout the reaction than those on other zeolites and amorphous SiO<sub>2</sub>. In addition, no appreciable difference in the isomer ratios of 2,4-DCT/3,4-DCT is observed with the progress of the reaction over these catalysts, however, the ratio of 2,4-DCT/3,4-DCT over FeCl<sub>3</sub> and K-L becomes nearly equal at about 80 wt% conversion level of 4-CT. The increase in the ratio over non-shape selective FeCl<sub>3</sub> during the reaction may be attributed to the formation of larger amounts of consecutive products at the expense of primary

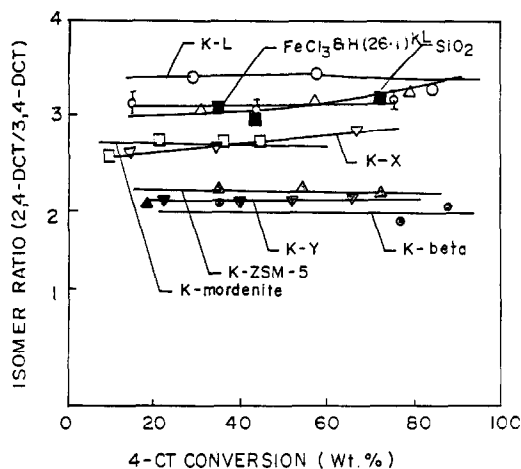


Fig. 2. 2,4-DCT/3,4-DCT isomer ratio as a function of 4-CT conversion. Reaction conditions: catalyst (g/mol 4-CT) = 3.78; Reaction temperature (K) = 368; 4-CT (mol) = 0.2;  $\text{Cl}_2$  flow (mol/h) = 0.09.

products [15]. These results and the earlier reports reveal that zeolite K-L plays a significant role in controlling the 2,4-DCT/3,4-DCT isomer ratio [11,28].

### 3.4. Effect of reaction time using zeolite K-L

The performance of the zeolite K-L catalyst at 368 K in terms of 4-CT conversion, product yields and ratio of 2,4-DCT/3,4-DCT as a function of time on stream is presented in Fig. 3. Both the conversion of 4-CT and the product yields increase with the duration of the run, whereas the isomer ratio of 2,4-DCT/3,4-DCT remains unchanged. The level of 4-CT conversion and yield for 2,4-DCT are determined to be 83.3 wt% and 51.6 wt%, respectively, after 3 h of the run. A sharp increase in the yield of others (polychlorinated products) is noticed after 3 h on stream due to the higher conversion of 4-CT and consequently the formation of polychlorinated toluenes by consecutive reactions [15,20].

### 3.5. Effect of solvent

The nature of reaction medium is also an important parameter as the solvent affects the

isomer ratio, product yields and the rate of 4-CT conversion. The results on the rate of 4-CT conversion, product yields and on the 2,4-DCT/3,4-DCT isomer ratio for the chlorination of 4-CT over zeolite K-L in  $\text{CH}_2\text{Cl}_2$ ,  $\text{ClCH}_2\text{CH}_2\text{Cl}$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$  and in the absence of any solvent are shown in Table 3.  $\text{CH}_2\text{Cl}_2$  appears to be the best solvent at 313 K and the isomer ratio of 2,4-DCT/3,4-DCT is found to be 4.1. The other solvents are not found to be effective enough at 313 K to give higher isomer ratio than the values obtained even in the neat chlorination of 4-CT (2,4-DCT/3,4-DCT = 3.5). More satisfactory reaction rates are obtained by raising the reaction temperature, which has no significant effect on the 2,4-DCT/3,4-DCT, except in the case of  $\text{ClCH}_2\text{CH}_2\text{Cl}$ . At higher temperature,  $\text{ClCH}_2\text{CH}_2\text{Cl}$  acts as the best solvent. As the temperature is raised from 313 to 353 K in the presence of  $\text{ClCH}_2\text{CH}_2\text{Cl}$ , the rate of 4-CT conversion increases from 9.4 to 28.3  $\text{mmol g}^{-1} \text{h}^{-1}$  and the ratio of 2,4-DCT/3,4-DCT increases from 3.6 to 4.3, respectively. The corresponding yield of 2,4-DCT also increases from 13.4 to 43.9 wt%, respec-

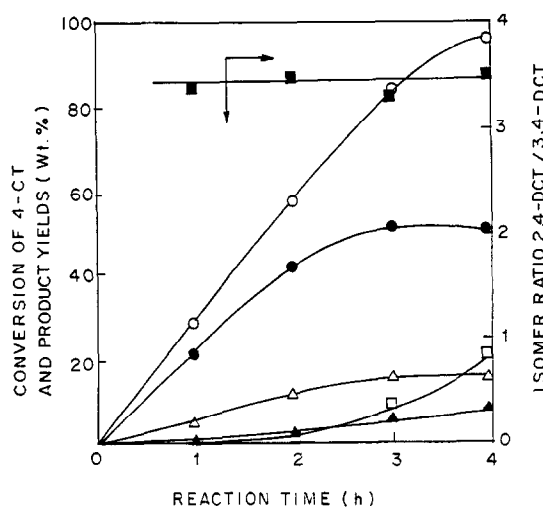


Fig. 3. Effect of reaction time on the conversion of 4-CT (○), 2,4-DCT/3,4-DCT (■) and product yields, 2,4-DCT (●), 3,4-DCT (△),  $\alpha$ ,4-DCT (▲) and others (□). Reaction conditions: Zeolite K-L (g/mol 4-CT) = 3.78; reaction temperature (K) = 368; 4-CT (mol) = 0.2;  $\text{Cl}_2$  flow (mol/h) = 0.09.

Table 3  
Solvent effect <sup>a</sup>

Solvent	Reaction temp (K)	Conv. of 4-CT (wt%)	Rate of 4-CT conv. <sup>b</sup> (mmol g <sup>-1</sup> h <sup>-1</sup> )	Product yields (wt%) <sup>c</sup>				2,4-/3,4- <sup>d</sup> isomer ratio
				2,4-DCT	3,4-DCT	$\alpha$ ,4-DCT	others	
CH <sub>2</sub> Cl <sub>2</sub>	313	40.1	19.8	27.1	6.6	3.9	2.5	4.1
ClCH <sub>2</sub> CH <sub>2</sub> Cl	353	57.2	28.3	43.9	10.1	2.1	1.1	4.3
ClCH <sub>2</sub> CH <sub>2</sub> Cl	313	19.0	9.4	13.4	3.7	1.1	0.8	3.6
CHCl <sub>3</sub>	333	37.6	18.6	24.2	6.8	4.5	2.1	3.6
CHCl <sub>3</sub>	313	25.2	12.5	12.8	3.6	7.7	1.1	3.6
CCl <sub>4</sub>	348	92.8	45.8	61.6	17.6	3.2	10.4	3.5
CCl <sub>4</sub>	313	47.8	23.6	30.5	8.6	5.3	3.4	3.5
No solvent <sup>e</sup>	368	57.3	75.5	41.8	11.8	1.9	1.8	3.5
No solvent <sup>e</sup>	313	51.4	67.7	37.9	10.7	1.3	1.5	3.5

<sup>a</sup> Reaction conditions: Catalyst (K-L) = 10.1g/mol 4-CT; 4-CT = 0.1mol; solvent = 12.5g; Cl<sub>2</sub> flow = 0.09 mol/h; Reaction time = 2 h.

<sup>b</sup> Initial rate of 4-CT conversion (mmol g<sup>-1</sup> h<sup>-1</sup>) is defined as mass of 4-CT converted/(mass of catalyst used) × (reaction time) h<sup>-1</sup>.

<sup>c</sup> 2,4-DCT = 2,4-dichlorotoluene; 3,4-DCT = 3,4-dichlorotoluene;  $\alpha$ ,4-DCT =  $\alpha$ ,4-dichlorotoluene; others = tri- and tetra-chlorotoluenes.

<sup>d</sup> Isomer ratio of 2,4-DCT/3,4-DCT.

<sup>e</sup> Reaction conditions same as in Table 2.

tively. The 2,4-DCT/3,4-DCT isomer ratio in different solvents is found to be in the order:



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



It has been reported earlier [28,31] that in the chlorination reactions solvents do not act only as a diluent. Botta et al. [28], Nakamura et al. [31] and Singh et al. [18,20] observed that solvents like CH<sub>2</sub>Cl<sub>2</sub> and ClCH<sub>2</sub>CH<sub>2</sub>Cl favour the

formation of para-products in the chlorination of aromatics over zeolite K-L. They suggested that these solvents may influence the activation of the reactants, diffusion and transport processes in the zeolite channels. In our study, CH<sub>2</sub>Cl<sub>2</sub> and ClCH<sub>2</sub>CH<sub>2</sub>Cl may be influencing the product ratio in a similar way.

### 3.6. Effect of partial cation-exchange

The results for chlorination of 4-CT over K-L modified with H<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, Cs<sup>+</sup>, and La<sup>+3</sup>

Table 4  
Effect of alkali cation-exchanged K-L zeolite <sup>a</sup>

Catalysts	conv. of 4-CT (wt%)	Rate of 4-CT conv. <sup>b</sup> (mmol g <sup>-1</sup> h <sup>-1</sup> )	Product yields (wt%) <sup>c</sup>				2,4-/3,4- <sup>d</sup> isomer ratio
			2,4-DCT	3,4-DCT	$\alpha$ ,4-DCT	others	
H (26.1) K-L <sup>e</sup>	73.1	96.3	49.2	14.7	2.9	6.3	3.3
Li (12.1) K-L <sup>e</sup>	72.9	96.0	47.3	15.0	3.8	6.8	3.2
Na (9.8) K-L <sup>e</sup>	70.0	92.2	44.8	14.3	5.3	5.6	3.1
K-L	57.3	75.5	41.8	11.8	1.9	1.8	3.5
Cs (21.1) K-L <sup>e</sup>	66.9	88.1	39.1	14.0	9.0	4.8	2.8
La (3.7) K-L <sup>e</sup>	61.9	81.5	39.7	12.9	4.0	5.3	3.1

<sup>a</sup> Reaction conditions: Catalyst = 3.78 g/mol 4-CT; 4-CT = 0.2 mol; reaction temperature = 368 K; Cl<sub>2</sub> flow = 0.09 mol/h.

<sup>b</sup> Initial rate of 4-CT conversion (mmol g<sup>-1</sup> h<sup>-1</sup>) is defined as mass of 4-CT converted/(mass of catalyst used) × (reaction time) h<sup>-1</sup>.

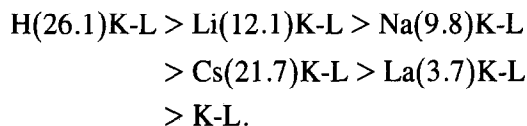
<sup>c</sup> 2,4-DCT = 2,4-dichlorotoluene; 3,4-DCT = 3,4-dichlorotoluene;  $\alpha$ ,4-DCT =  $\alpha$ ,4-dichlorotoluene; others = tri- and tetra-chlorotoluenes.

<sup>d</sup> Isomer ratio of 2,4-DCT/3,4-DCT.

<sup>e</sup> Values in parentheses correspond to percent of the particular cation in zeolite K-L.

Reaction time = 2 h.

are presented in Table 4. A comparison of the results for K-L with these catalysts indicates a significant change in the rate of 4-CT conversion. The data presented in Table 4, reveal that the activity (rate of 4-CT conversion) of catalysts in facilitating the reaction of 4-CT with  $\text{Cl}_2$  gas decreases in the order:



It is proposed that the chlorine molecule is polarized by zeolites and then attacks the aromatic ring for the electrophilic chlorination of aromatics and, hence, the rate of polarization of  $\text{Cl}_2$  molecule over catalysts affects the rate of 4-CT conversion. Sekizawa et al. [32] reported that the polarization of  $\text{Cl}_2$  molecule is diminished by the decrease in acid strength of catalysts by alkali metals. However, zeolite K-L exchanged with  $\text{Cs}^+$  behaves quite differently as it is more active and less selective than the unmodified zeolite K-L (Table 4). In contrast to other exchanged catalysts except K-L,  $\text{La}(3.7)\text{K-L}$  exhibits lower activity in the chlorination of 4-CT. These results are in agreement with the earlier reports [32].

### 3.7. Effect of catalyst concentration

The effect of catalyst concentration in the range of 0 to 5 g/mol of 4-CT on the conversion of 4-CT, product yields and isomer ratio of 2,4-DCT/3,4-DCT is studied at 363 K for 1 h of reaction time in the chlorination of 4-CT over zeolite K-L (Fig. 4). The different ratios of catalyst to 4-CT are obtained by varying the amount of the zeolite K-L and keeping the concentration of 4-CT constant. As expected, only side-chain chlorinated product is produced in the absence of catalyst [18,26]. The conversion of 4-CT steadily increases from 17.3 to 28.7 wt% with increasing catalyst concentration from 1.26 to 3.80 g/mol of 4-CT, respectively. Beyond 3.8 g catalyst/mol of 4-CT, the conversion of 4-CT remains constant. The isomer ratio

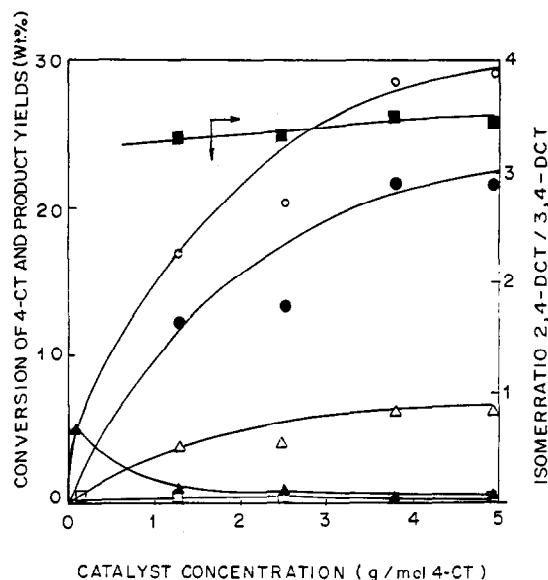


Fig. 4. Effect of catalyst K-L concentration on the conversion of 4-CT (○), 2,4-DCT/3,4-DCT (■) and product yields; 2,4-DCT (●), 3,4-DCT (△),  $\alpha$ ,4-DCT (▲) and others (□). Reaction conditions: reaction temperature (K) = 363; 4-CT (mol) = 0.2;  $\text{Cl}_2$  flow (mol/h) = 0.09; reaction time (h) = 1.

of 2,4-DCT/3,4-DCT shows nearly the same trend upon increasing the catalyst/4-CT ratio. Enhancement in the 4-CT conversion with the increase in the catalyst concentration may be attributed to the increase in the total number of active sites which polarize the  $\text{Cl}_2$  molecule for the nuclear chlorination of 4-CT.

### 3.8. Effect of reaction temperature

The effect of the reaction temperature on the rate of 4-CT conversion, product yields and isomer ratio of 2,4-DCT/3,4-DCT is illustrated in Fig. 5. The rate of 4-CT conversion increases steadily with temperature in zeolite K-L. However, the isomer ratio of 2,4-DCT/3,4-DCT decreases with increase in the reaction temperature from 328 to 413 K.

### 3.9. Effect of HCl treatment on zeolite K-L

Table 5 reports the catalytic activity of K-L samples with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios in the chlorination of 4-CT. The various dealuminated



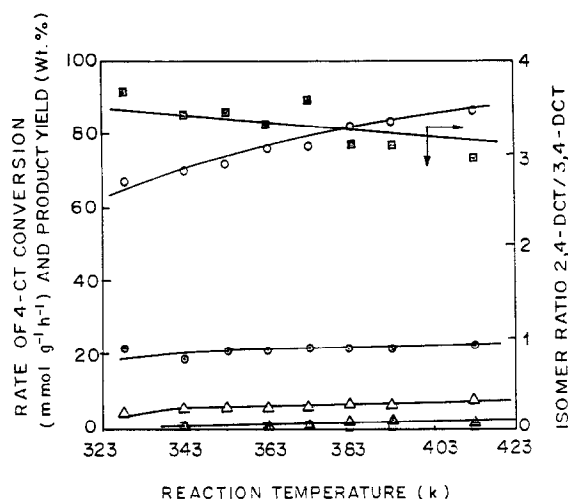


Fig. 5. Effect of reaction temperature on the rate of 4-CT conversion (○), 2,4-DCT/3,4-DCT (■) and product yields; 2,4-DCT (●), 3,4-DCT (△),  $\alpha$ ,4-DCT (▲) and others (□). Reaction conditions: zeolite K-L (g/mol 4-CT) = 3.78; 4-CT (mol) = 0.2; Cl<sub>2</sub> flow (mol/h) = 0.09; reaction time (h) = 1.

samples of K-L are obtained by the treatment of parent K-L with different molar solutions of HCl (0.05 to 0.7 M HCl). In order to check the structure and crystallinity of the catalysts after HCl treatment, X-ray powder diffraction patterns are recorded. XRD measurements indicate that the HCl treated samples retain the K-L structure. However, the crystallinity of K-L(0.5) and K-L(0.7) is reduced to some extent (Table

5). It can be seen that the rate of 4-CT conversion and product composition are not greatly affected over K-L, K-L(0.05), K-L(0.1), and K-L(0.3) samples. Whereas, K-L(0.5) and K-L(0.7) which are obtained by increasing the dealumination of the same starting material (K-L), display lower activity, selectivity (2,4-DCT/3,4-DCT ratio) and formation of large amounts of side-chain chlorinated product ( $\alpha$ ,4-DCT) (Table 5). The rate of 4-CT conversion (mmol g<sup>-1</sup> h<sup>-1</sup>) decreases in the order: K-L > K-L(0.05) > K-L(0.1) > K-L(0.3) > K-L(0.5) > K-L(0.7).

The decrease in this order may be ascribed to the increase in the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio and consequently decrease in the number of basic sites of the zeolite K-L. The lower activity and formation of large amount of  $\alpha$ ,4-DCT over K-L(0.5) and K-L(0.7) may be attributed to their higher SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios and lower crystallinity compared to the other zeolite K-L samples.

### 3.9.1. Catalyst recycling

Zeolite K-L is recycled in five runs for the chlorination of 4-chlorotoluene at identical reaction conditions to examine the stability of the catalyst. The used catalyst is activated each time at 773 K in the presence of air and characterized for its chemical composition and crystallinity

Table 5  
Effect of HCl treated zeolite K-L<sup>a</sup>

Catalyst	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (molar ratio)	Conv. of 4-CT (wt%)	Rate of 4-CT conv. <sup>b</sup> (mmol g <sup>-1</sup> h <sup>-1</sup> )	Product yields (wt%) <sup>c</sup>				2,4-/3,4- <sup>d</sup> isomer ratio	Crystallinity (%)
				2,4-DCT	3,4-DCT	$\alpha$ ,4-DCT	others		
K-L	6.82	57.3	75.5	41.8	11.8	1.9	1.8	3.5	100
K-L (0.05) <sup>e</sup>	7.43	54.8	72.2	40.0	11.3	1.8	1.7	3.5	100
K-L (0.1) <sup>e</sup>	8.02	53.6	70.6	39.1	11.0	1.8	1.7	3.5	100
K-L (0.3) <sup>e</sup>	8.63	52.5	69.2	38.3	10.8	1.7	1.7	3.5	100
K-L (0.5) <sup>e</sup>	8.73	45.9	60.5	25.9	7.7	11.1	1.2	3.4	83.3
K-L (0.7) <sup>e</sup>	9.01	39.9	52.6	22.4	7.2	9.4	0.9	3.1	44.4

<sup>a</sup> Reaction conditions: Catalyst = 3.78 g/mol 4-CT; 4-CT = 0.2 mol; reaction temperature = 368 K; Cl<sub>2</sub> flow = 0.09 mol/h.

<sup>b</sup> Initial rate of 4-CT conversion (mmol g<sup>-1</sup> h<sup>-1</sup>) is defined as mass of 4-CT converted/(mass of catalyst used) × (reaction time) h<sup>-1</sup>.

<sup>c</sup> 2,4-DCT = 2,4-dichlorotoluene; 3,4-DCT = 3,4-dichlorotoluene;  $\alpha$ ,4-DCT =  $\alpha$ ,4-dichlorotoluene; others = tri- and tetra-chlorotoluenes.

<sup>d</sup> Isomer ratio of 2,4-DCT/3,4-DCT.

<sup>e</sup> Values in parentheses correspond to the molarity of HCl solution taken for K-L treatment; percentage of K-exchange in each sample > 98.

Reaction time = 2 h.

Table 6  
Catalyst recycling <sup>a</sup>

Recycle	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (molar ratio)	Degree of K <sup>+</sup> - in zeolite (%)	Conv. of 4-CT (wt%)	Rate of <sup>b</sup> 4-CT conv. (mmol g <sup>-1</sup> h <sup>-1</sup> )	Product yields (wt%) <sup>c</sup>				2,4-/3,4- <sup>d</sup> isomer ratio	Crystallinity of K-L(%)
					2,4-DCT	3,4-DCT	α,4-DCT	others		
0 (fresh)	6.82	> 98.0	57.3	75.8	41.8	11.8	1.9	1.8	3.5	100
1st	6.90	97.9	52.0	68.5	35.6	11.0	2.8	2.6	3.2	—
2nd	7.04	96.2	51.5	67.8	34.2	10.6	4.6	2.1	3.2	—
3rd	7.15	94.4	50.4	66.4	32.9	10.5	5.2	1.8	3.1	—
4th	7.26	93.0	50.3	66.3	33.0	10.1	5.7	1.5	3.2	—
5th	7.43	91.7	50.0	65.9	30.5	9.4	6.8	3.3	3.2	84.5

<sup>a</sup> Reaction conditions: Catalyst = 3.78 g/mol 4-CT; 4-CT = 0.2 mol; reaction temperature = 368 K; Cl<sub>2</sub> flow = 0.09 mol/h.

<sup>b</sup> Initial rate of 4-CT conversion (mmol g<sup>-1</sup> h<sup>-1</sup>) is defined as mass of 4-CT converted/(mass of catalyst used) × (reaction time) h<sup>-1</sup>.

<sup>c</sup> 2,4-DCT = 2,4-dichlorotoluene; 3,4-DCT = 3,4-dichlorotoluene; α,4-DCT = α,4-dichlorotoluene; others = tri- and tetra-chlorotoluenes.

<sup>d</sup> Isomer ratio of 2,4-DCT/3,4-DCT.

Reaction time = 2 h.

(Table 6, Fig. 6). The general recycling results in Table 6 demonstrate a lower activity (rate of 4-CT conversion). However, the 2,4-DCT/3,4-DCT isomer ratios are quite similar to that for the fresh catalyst. From first to fifth recycle, the rate of 4-CT conversion decreases slowly but there is an increase in the formation of the side-chain chlorinated product, α,4-DCT. The results of the chemical composition and the XRD of the catalysts show that the loss of activity and the enhancement in the amount of α,4-DCT over K-L with the increase in the number of cycles may be correlated with the slight increase in the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, decrease in degree of K<sup>+</sup>- exchange and reduction

in relative crystallinity (Fig. 6). The hydrogen chloride produced in the electrophilic chlorination of 4-CT is responsible for the deactivation of the K-L. These results are consistent with the earlier report [15,18].

#### 4. Conclusions

In conclusion, zeolite K-L has been found superior compared to other zeolites studied and the conventional Lewis acid catalyst, FeCl<sub>3</sub>, in catalyzing the chlorination of 4-chlorotoluene with Cl<sub>2</sub> gas effectively to obtain high selectivity (ratio of 2,4-DCT/3,4-DCT) for 2,4-dichlo-

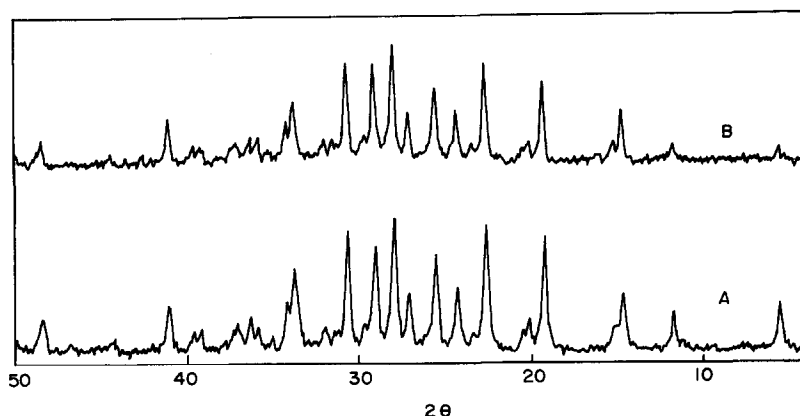


Fig. 6. X-ray diffraction patterns of fresh K-L (A) and K-L recycled the fifth time (B).

rotoluene. The acidic H(26.1)K-L exhibits higher rate of 4-CT conversion than those of basic K-L and  $\text{FeCl}_3$ . The Lewis acid catalyst  $\text{FeCl}_3$ , produces higher amounts of polychlorinated products compared to the zeolite catalysts.  $\alpha$ ,4-DCT is achieved in larger amounts over K-X, amorphous  $\text{SiO}_2$  and in the absence of any catalyst. Among the solvents, 1,2-dichloroethane gives the highest selectivity for 2,4-dichlorotoluene over K-L at 353 K. Partial modification of the zeolite K-L with  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Cs}^+$  and  $\text{La}^{+3}$  cations increases the rate of 4-CT conversion. The yield of the 2,4-DCT increases with the increase in the reaction time, amount of the catalyst K-L and reaction temperature. However, the change in the isomer ratio (2,4-DCT/3,4-DCT) is found to be negligible. Further, the rate of 4-CT conversion decreases with the increase in the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of zeolite K-L (obtained by HCl treatment). The decrease in the activity (deactivation of K-L) with the recycling experiments may be attributed in part to the changes in chemical composition and crystallinity of zeolite K-L by HCl (produced as a by product in the reaction). Presumably, the reaction appears to proceed by an electrophile ( $\text{Cl}^+$ ), followed by the interaction of  $\text{Cl}^+$  with the 4-CT, resulting in the dichlorotoluenes.

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