

A catalytic method for the selective chlorination of benzyl chloride to 4-chlorobenzyl chloride using zeolite catalysts

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Abstract

The liquid phase chlorination of benzyl chloride (BC) has been investigated in the presence of a series of zeolite catalysts at 353 K under atmospheric pressure. A comparative study of these catalysts reveals that zeolite K-L exhibits the higher rate of BC conversion ($76.4 \text{ mmol g}^{-1} \text{ h}^{-1}$), except H(26.1)K-L ($98.4 \text{ mmol g}^{-1} \text{ h}^{-1}$) and higher selectivity for 4-chlorobenzyl chloride (4-CIBC/2-CIBC = 3.7) than the other zeolite catalysts. The absence of any catalyst, zeolites K-X and K-Y mainly promote the side chain chlorination of BC to α, α -dichlorotoluene. The effects of reaction time, solvents, catalyst concentration and reaction temperature are also examined. A combination of solvent and reaction temperature not only affect the rate of BC conversion, but also enhance markedly, the isomer ratio of 4-CIBC/2-CIBC. 1,2-Dichloroethane is the best solvent and the isomer ratio of 4-CIBC/2-CIBC and the rate of BC conversion over zeolite K-L are enhanced from 2.21 to 7.21 and 13.2 to $51.9 \text{ mmol g}^{-1} \text{ h}^{-1}$ (in the presence of solvent), respectively, when the reaction temperature is raised from 313 to 353 K. Further, the use of 1,2-dichloroethane as solvent in the reaction decreases the formation of side chain and consecutive products significantly. As the reaction time and amount of the catalyst in the reaction mixture are increased, an increase in the conversion of benzyl chloride is noticed. The zeolite K-L is recycled three times with a decline in catalytic activity. The probable mechanism involves the formation of an electrophile (Cl^+) from Cl_2 gas over zeolite catalyst which react with BC to form the ring chlorinated products. © 1999 Elsevier Science B.V. All rights reserved.

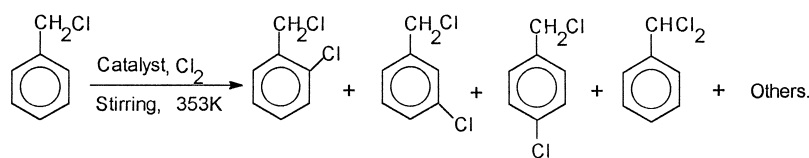
Keywords: Chlorination of benzyl chloride; 4-Chlorobenzyl chloride; Zeolite catalysts

1. Introduction

4-Chlorobenzyl chloride is an intermediate in the manufacture of rice herbicide, 'Saturn' ((*S*-4-chlorobenzyl) *N,N*-diethylthiol carbamate) [1,2]. The ring chlorinated benzyl chlorides are also used in the preparation of quaternary ammonium salts and as intermediates for pharmaceuticals and pesticides [2]. Conventionally, the

4-chlorobenzyl chloride is produced by the direct side chain chlorination of *para*-chlorotoluene (PCT). Further, in the presence of an iodine catalyst, chlorination of benzyl chloride yields a mixture consisting mostly of the 2-chloro- and 4-chlorobenzyl chlorides (2-CIBC and 4-CIBC) in equal amounts [2]. With strong Lewis acid catalysts such as ferric chloride, chlorination is accompanied by self-condensation [2]. Industrially, these reported methods for the production of 4-CIBC are not attractive owing to the use of expensive PCT and

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Scheme 1.

lower regioselectivity of iodine catalyst. In view of the above, it was of interest to develop a new solid catalyst for the selective synthesis of 4-chlorobenzyl chloride. Zeolites are widely used as selective catalysts particularly in the petrochemical industry [3–5]. However, their use in finer organic synthesis has been very limited. In recent times there has been a wider recognition of the potential of zeolites for fine chemical synthesis and recently increasing attention is being paid to such possibilities [6,7]. More recently, zeolites have been used in the selective halogenation of aromatics [8–20], however, their properties have not been exploited so far in the selective chlorination of BC to 4-CIBC. The aim of the present work is to enhance the yield of 4-CIBC and to reduce the formation of side-chain and consecutive products in the chlorination of BC over zeolite catalysts. We report herein, for the first time, a catalytic method for the regioselective chlorination of BC to 4-CIBC under mild reaction conditions using zeolites as catalyst and chlorine gas as the chlorinating agent (Scheme 1). The influence of catalyst concentration, solvent and reaction temperature is also examined on the rate of benzyl chloride conversion, product yields and ratio of 4-CIBC/2-CIBC.

2. Experimental

Zeolites beta, ZSM-5 and K-L samples used in this study were synthesized hydrothermally as per the literature procedures [21,22]. The crystalline product thus obtained was filtered, washed with distilled water, dried and calcined at 773 K for 16 h in the presence of air. The K-forms of these zeolites were prepared by a

conventional ion-exchange method, in which the zeolites were treated thrice in an aqueous solution of KNO_3 (1 M) at 353 K for 8 h and washed with deionized water, filtered and dried at 383 K for 2 h. Zeolite H(26.1)K-L was prepared by stirring 5 g of the K-L sample in 50 ml of an aqueous solution of 0.1 M NH_4NO_3 for 24 h at 303 K. The resulting sample was washed with deionized water, dried and calcined at 773 K for 12 h. Zeolites H-mordenite, Na-Y and Na-X were supplied by Laporte Inorganics, Cheshire, UK. These zeolites were converted into their K-forms following the above exchange conditions.

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and the degree of ion-exchange of the zeolites were determined by a combination of wet and atomic absorption methods (Hitachi 800). The crystallinity of the samples was evaluated by the X-ray diffractometer (Rigaku, D-Max/III-VC model) using $\text{CuK}\alpha$ radiation. XRD examination gave no evidence of structure or crystallinity change of the samples as a result of the treatment with NH_4NO_3 or KNO_3 . The BET surface area data were obtained from the Nitrogen adsorption. The crystal size of the zeolites was determined by using a scanning electron microscope (Shimadzu, Model UV-2101 PC). All catalysts were activated at 473 K for 2 h prior to the reaction. The main properties of the zeolites are summarized in Table 1.

The catalytic runs were carried out batchwise in a mechanically stirred, closed 100 ml glass reactor fitted with a reflux condenser, a thermometer, a N_2/Cl_2 gas-line and a septum for withdrawing the samples. In a typical run, an amount of benzyl chloride (0.158 mol in the neat chlorination and 0.08 mol in the presence of 10 ml solvent) was charged in the reactor

Table 1
Properties of zeolites

Zeolite	SiO ₂ /Al ₂ O ₃ (molar ratio)	Cation composition (%) ^a			Surface area ^b (m ² /g)	Crystal size (μm)
		H ⁺	Na ⁺	K ⁺		
K-X	2.4	–	7.4	92.6	615	1.0
K-Y	4.1	–	7.2	92.8	606	1.0
K-mordenite	22.0	7.5	2.7	89.8	542	1.0
K-ZSM-5	41.0	2.5	1.4	96.1	410	0.5
K-beta	26.0	9.8	4.3	85.9	743	0.5
H(26.1)K-L ^c	6.8	26.1	–	73.9	221	0.2
K-L	6.8	–	1.4	98.6	215	0.2

^aNa⁺ and K⁺ ions were analyzed 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 cation sites with aluminum content taken as 100%.

^bMeasured by the N₂ adsorption.

^cValue in parentheses represents the percentage of H⁺ in K-L.

along with the appropriate amount of activated catalyst. The reaction mixture was heated to the required temperature under stirring in the presence of N₂ (20 ml/min) for 30 min. Then N₂ gas was stopped and the reaction was started by passing Cl₂ gas (0.09 mol/h). Aliquots were removed at various time intervals, filtered, neutralized with NaHCO₃ and analyzed by gas chromatograph (Blue-star Model 421, equipped with a flame ionization detector and a capillary column, 50 m × 0.2 mm with methyl silicone gum). Products were identified by GC-MS and with reference to standard samples.

The conversion is defined as the percentage of BC transformed. The rate of BC conversion (mmol g⁻¹ h⁻¹) was calculated as the amount of BC (mmol) converted per hour over per g of the catalyst. The yield percentage of a product represents the amount of the product calculated from the selectivity multiplied by the conversion.

3. Results and discussion

3.1. Influence of various catalysts

Table 2 compares the rate of benzyl chloride conversion, product yields and the ratio of 4-CIBC/2-CIBC over various zeolites such as H(26.1)K-L, K-L, K-beta, K-mordenite, K-

ZSM-5, K-Y, K-X and in the absence of catalyst in the chlorination of benzyl chloride at 353 K under similar reaction conditions. The reaction produces a mixture of 2-chlorobenzyl chloride (2-CIBC), 3-chlorobenzyl chloride (3-CIBC), 4-chlorobenzyl chloride (4-CIBC) and side chain chlorinated product, α,α-dichlorotoluene (α,α-DCT). The small percentage of consecutive products (others) is also detected. The formation of mono-chlorobenzyl chlorides takes place by parallel reaction while di- and tri-chlorobenzyl chlorides are obtained by consecutive reactions of the mono-chlorobenzyl chlorides [15,18]. The most interesting feature of the reaction is that the rate of benzyl chloride conversion, product yields and the 4-CIBC/2-CIBC ratio depend on the type of zeolite used. As can be seen from the Table 2, zeolites H(26.1)K-L, K-L and K-beta produce predominantly nuclear chlorinated products while the blank experiment (without catalyst), zeolites K-ZSM-5, K-mordenite, K-Y and K-X exhibit mainly the side chain chlorinated product. The highest yield of α,α-DCT was observed over the zeolite K-X (Table 2) which is in agreement with the previous literature and may be ascribed to the lower SiO₂/Al₂O₃ ratio than the other zeolites [23,24]. Delaude and Laszlo [23] has reported that O₃SiOAlO₃ network of the zeolite undergoes homolytic opening into O₃SiO· + O₃Al· favouring the formation of side-chain

Table 2
Chlorination of benzyl chloride^a

Catalyst	Reaction time (h)	Conversion of BC (wt.%)	Rate of BC conversion ^b (mmol g ⁻¹ h ⁻¹)	Product yields (wt.%) ^c					4-/2- ^d ratio
				2-CIBC	3-CIBC	4-CIBC	α, α-DCT	Others	
None	1	15.1	–	–	–	–	15.1	–	–
	3	41.7	–	–	1.3	0.2	40.2	–	–
K-ZSM-5	1	11.3	37.2	0.5	0.1	0.5	9.4	0.8	1.0
	3	35.2	–	1.0	0.3	1.0	32.5	0.4	1.0
K-mordenite	1	11.4	37.5	0.5	0.1	0.5	10.2	0.1	1.0
	3	46.5	–	0.8	0.2	0.7	44.0	0.8	0.9
K-X	1	15.2	50.0	0.1	0.0	0.0	14.6	0.5	–
	3	61.3	–	0.2	0.0	0.1	59.1	1.9	–
K-Y	1	14.4	47.4	0.3	0.1	0.3	13.6	0.1	1.0
	3	48.1	–	0.8	0.1	0.5	46.0	0.7	0.62
K-beta	1	14.3	47.1	3.5	1.1	7.8	1.7	0.2	2.20
	3	34.4	–	7.1	2.1	13.5	11.2	0.5	1.90
H(26.1)K-L ^e	1	29.9	98.4	6.8	3.5	15.5	4.1	–	2.30
	3	70.1	–	10.5	4.5	37.2	14.1	3.8	3.54
K-L	1	23.2	76.4	3.3	1.4	12.2	5.9	0.4	3.70
	3	55.7	–	6.6	2.7	23.3	21.5	1.6	3.53

^aReaction conditions: catalyst (g/mol BC) = 3; reaction temperature (K) = 353; BC (mol) = 0.158; Cl₂ flow (mol/h) = 0.09; Reaction time (h) = 3.

^bRate of BC conversion is expressed as, amount of BC converted/weight of the catalyst × reaction time (h).

^c2-CIBC = 2-chlorobenzyl chloride; 3-CIBC = 3-chlorobenzyl chloride; 4-CIBC = 4-chlorobenzyl chloride; α,α-DCT = α,α-dichlorotoluene; Others = di- and trichlorobenzyl chlorides.

^dIsomer ratio of 4-CIBC/2-CIBC.

^eSee footnote to Table 1.

product (α,α -DCT) through radical reactions. In addition, side chain chlorination of BC in the absence of any catalyst and poorly dark reaction conditions may be attributed to the photochlorination (by the free radical mechanism) of $-\text{CH}_2\text{Cl}$ group of benzyl chloride [23,25].

The results demonstrate that zeolite K-L is more active and highly selective and both, the rate of benzyl chloride conversion ($76.4 \text{ mmol g}^{-1} \text{ h}^{-1}$) and the isomer ratio (4-CIBC/2-CIBC = 3.7) are found to be far superior over K-L compared to the other zeolites except H(26.1)K-L after one hour of reaction time. The acidic H(26.1)K-L gave higher rate of BC conversion ($98.4 \text{ mmol g}^{-1} \text{ h}^{-1}$) and lower amount of the side chain chlorinated product (α,α -DCT) [23] compared to the K-L (Table 2). It is confirmed from these results that the conventional concept of geometry related shape selectivity cannot be related alone to explain the role of zeolite K-L in enhancing the *para*-selectivity (ratio of 4-CIBC/2-CIBC) in the chlorination of benzyl chloride. It is seen that zeolites of similar pore diameter but of different structural types behave in different ways [8,12]. In addition, Wortel et al. [15] (in the bromination of halobenzenes), Botta et al. [12] (in the chlorination of biphenyl) and Singh et al. [18] (in the chlorination of toluene) suggested that factors such as size, charge and position of the cations and electrostatic forces produced by them in the zeolite channels direct the substitution to get the higher selectivity for *para*-products. It is also observed by Van Dijk et al. [9] that highly selective *para*-substitution in the halogenation of aromatics over zeolite catalysts may be attributed to a specific orientation of the substrate in the cavities of the zeolites resulting in steric hindrance at the *ortho* position and activation of the *para*-position by electrostatic influences in the zeolite crystals.

The combined effect of all these factors may be responsible for the polarization of Cl_2 molecule and the selective formation of 4-CIBC over zeolite K-L in the chlorination of benzyl chloride.

3.2. Influence of duration of the run on the conversion of BC over various catalysts

The effect of duration of run on the performance of various catalysts, under identical reaction conditions in the chlorination of BC is also tested. Increasing reaction time increased the conversion of BC over all catalysts (Fig. 1). H(26.1)K-L yielded a considerably superior performance through out the reaction and its activity is found to be higher compared with other zeolite catalysts. The reason could be the higher acidity of H(26.1)K-L [23,24]. The activity order of various zeolite catalysts after 3 h of reaction time is as follows: H(26.1)K-L > K-L > K-X > K-Y > K-mordenite > K-ZSM-5 > K-beta

3.3. 4CIBC / 2-CIBC ratio vs. conversion

In Fig. 2, the isomer ratio of 4-CIBC/2-CIBC as a function of BC conversion (obtained over various catalysts in the chlorination of BC) is plotted. Such a representation gives information about the selectivity properties of the catalysts. The results show that zeolite K-L is more selective (4-CIBC/2-CIBC = 3.7) than the other catalysts and the ratio of 4-CIBC/2-CIBC does not

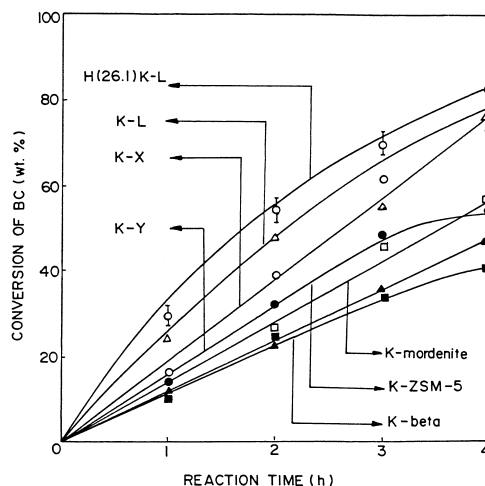


Fig. 1. Conversion of BC over zeolite catalysts vs. reaction time: reaction conditions: catalyst = 3.0 g/mol BC, BC (mol) = 0.158, reaction temperature (K) = 353, Cl_2 flow rate (mol/h) = 0.09

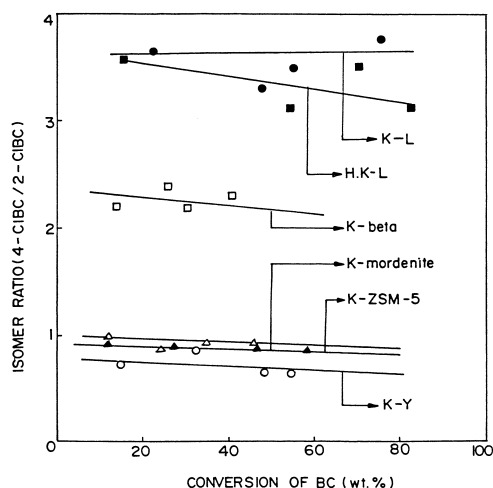


Fig. 2. 4-CIBC/2-CIBC isomer ratio vs. conversion of BC over various catalysts: reaction conditions as in Fig. 1.

change with the increase in BC conversion and it remains roughly almost constant over all catalysts. The selectivity of K-beta (4-CIBC/2-CIBC = 2.3) is found to be lower than K-L and H(26.1)K-L. Furthermore, the isomer ratio over K-mordenite, K-ZSM-5 and K-Y is found to be much lower (< 1.0) compared to the other zeolite catalysts. These results confirm that zeolite K-L plays a vital role in determining the isomer ratio of 4-CIBC/2-CIBC in the chlorination of BC. These results are in close agreement with the earlier reported data in the chlorination of toluene and 1,2-dichlorobenzene [18,20,24].

3.4. Influence of reaction time using zeolite K-L

A typical reaction course according to the time is pointed out in Fig. 3 for the transformation of BC over zeolite K-L at 353 K. The conversion of BC increased almost linearly with the reaction time. The results show that the reaction time influenced the conversion of BC, but did not affect the 4-CIBC/2-CIBC ratio to a greater extent.

3.5. Influence of solvent

The course of the liquid phase chlorination of aromatics over zeolite catalysts is greatly af-

ected by the type of the solvent used in the reaction [9,12,15,24]. The rate of benzyl chloride conversion ($\text{mmol g}^{-1} \text{h}^{-1}$), product yields and the isomer ratio of 4-CIBC/2-CIBC obtained in the chlorination of benzyl chloride using zeolite K-L in $\text{ClCH}_2\text{CH}_2\text{Cl}$, CHCl_3 , CCl_4 and in the absence of any solvent are shown in Table 3. Among the solvents used, the higher activity (rate of BC conversion) and selectivity (4-CIBC/2-CIBC) is observed in 1,2-dichloroethane. The rate of BC conversion and the 4-CIBC/2-CIBC isomer ratio at 313 K in the presence of 1,2-dichloroethane are found to be $13.2 \text{ mmol g}^{-1} \text{h}^{-1}$ and 2.21 respectively. The use of other solvents (CHCl_3 , CCl_4) has led to a lower selectivity for 4-CIBC and product yields when compared with 1,2-dichloroethane at similar reaction conditions at 313 K (Table 3). The rate of BC conversion at 313 K decreases by changing the solvent in the following order: $\text{ClCH}_2\text{CH}_2\text{Cl} > \text{CCl}_4 > \text{CHCl}_3$. The over all trend of the isomer ratio (4-CIBC/2-CIBC) in these solvents at 313 K is found to be in the order: $\text{ClCH}_2\text{CH}_2\text{Cl} > \text{CCl}_4 \cong \text{CHCl}_3$.

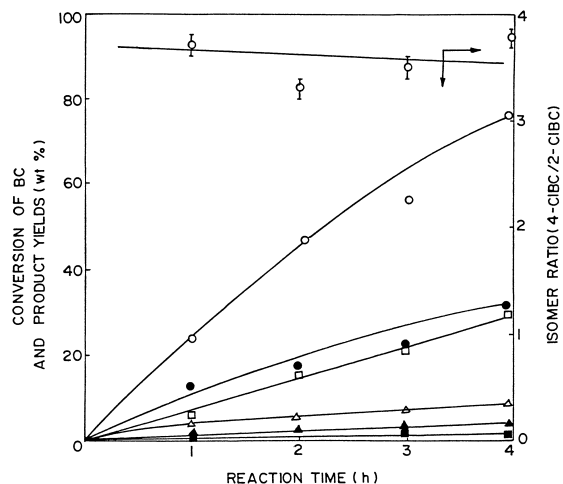


Fig. 3. Effect of reaction time on the conversion of BC (○), 4-CIBC/2-CIBC ratio (◇), and product yields, 4-CIBC (●), 2-CIBC (△), 3-CIBC (▲), α , α -DCT (□) and others (■); reaction conditions: catalyst (K-L) = 3.0 g/mol BC, BC (mol) = 0.158, reaction temperature (K) = 353, Cl_2 flow rate (mol/h) = 0.09.

Table 3
Solvent effect in the chlorination of BC over zeolite K-L^a

Solvent	Reaction temperature (K)	Conversion of BC (wt.%)	Rate of BC conversion ^c (mmol g ⁻¹ h ⁻¹)	Product yields (wt.%) ^d					4-/2- ^e ratio
				2-CIBC	3-CIBC	4-CIBC	α , α -DCT	Others	
ClCH ₂ CH ₂ Cl	313	13.4	13.2	1.4	0.3	3.1	6.6	2.0	2.21
ClCH ₂ CH ₂ Cl	353	52.6	51.9	5.7	3.5	41.1	1.8	0.5	7.21
CHCl ₃	313	2.8	2.8	0.6	0.2	0.5	1.0	0.5	0.83
CHCl ₃	333	9.2	9.1	1.1	–	5.6	2.2	0.3	5.09
CCl ₄	313	6.8	6.7	1.8	–	1.5	3.5	–	0.83
CCl ₄	348	23.2	22.9	4.7	1.3	13.3	3.9	–	2.82
No Solvent _f	313	14.8	48.7	3.0	0.6	8.4	2.1	0.7	2.80
No Solvent _f	353	23.2	76.4	3.3	1.4	12.2	5.9	0.4	3.69

^aReaction Conditions: catalyst = 10.1 g/mol BC; BC (mol) = 0.08; Cl₂ flow (mol/h) = 0.09; Reaction time (h) = 1; Solvent (ml) = 10.

^{c,d,e}see footnotes to Table 2.

^fReaction conditions similar as in Table 2.

Table 4
Catalyst recycling^a

Recycle	SiO ₂ /Al ₂ O ₃ (molar ratio)	Degree of K ⁺ -in zeolites (%)	Conv. of BC (wt.%)	Rate ^b of BC conv. (mmol g ⁻¹ h ⁻¹)	Product yields (wt.%) ^c					4-CIBC ^d /2-CIBC isomer ratio	Crystallinity of K-L (%)
					2-CIBC	3-CIBC	4-CIBC	α , α -DCT	Others		
0 (fresh)	6.82	98.6	59.8	59.0	9.51	3.7	30.1	12.7	3.9	3.2	100
1st	6.97	96.7	53.0	52.3	8.1	3.5	32.2	7.1	1.7	4.0	89
2nd	7.09	95.0	44.8	44.2	7.0	2.8	20.1	13.5	1.4	2.9	64.7
3rd	7.21	93.2	35.5	35.1	4.2	1.3	8.2	20.8	1.1	2.0	46.9

^aReaction conditions: catalyst (g/mol BC) = 5; reaction temperature (K) = 353; BC (mol) = 0.237; Cl₂ flow (mol/h) = 0.09; reaction time (h) = 2.

^{b,c,d}see footnotes to Table 2.

A significant enhancement in the rate of BC conversion and the 4-CIBC/2-CIBC isomer ratio is observed with the increase in the reaction temperature in the presence of all solvents. In addition, a twofold increase in the 4-CIBC/2-CIBC isomer ratio is noticed when the reaction is performed in 1,2-dichloroethane instead of neat chlorination at 353 K (Table 3). When the temperature is raised from 313 to 353 K in the presence of 1,2-dichloroethane, the rate of BC conversion and the isomer ratio of 4-CIBC/2-CIBC increased. Side-chain chlorination of BC to α,α -DCT to some extent is observed to be dependent on the reaction solvent. The more selective reaction in 1,2-dichloroethane at 353 K is found to yield lower concentration of α,α -DCT at higher conversion level of BC, whereas a higher amount of α,α -DCT, is obtained at lower conversion level of BC in the neat chlorination at 353 K (Table 3). Presumably, the higher dielectric constant (ionic medium) of the 1,2-dichloroethane favours the rupture of Cl-Cl bond into Cl^+ (electrophile) [29] and hence minimizes the formation of radical (Cl^\cdot) which enhances the side-chain chlorination of BC [23]. The higher 4-CIBC/2-CIBC isomer ratio observed in 1,2-dichloroethane in the chlorination of BC over zeolite K-L may be attributed to its higher polarity. In addition, others [12,30] have suggested that solvents may influence the activation of the reactants or affect the diffusion and transport process in the zeolite channels which may enhance the formation of 4-CIBC.

3.6. Influence of catalyst concentration

In order to clarify the effect of catalyst concentration on the conversion of BC, product yields and the ratio of 4-CIBC/2-CIBC, the catalyst (K-L) concentration was increased from 3.0 g/mol of BC to 5.0 g/mol of BC (Fig. 4). The total surface area available for the reaction depends on the catalyst loading. The conversion of BC increased and the formation of α,α -DCT is decreased when 5.0 g catalyst per mol of BC is used in the reaction because of the increase in

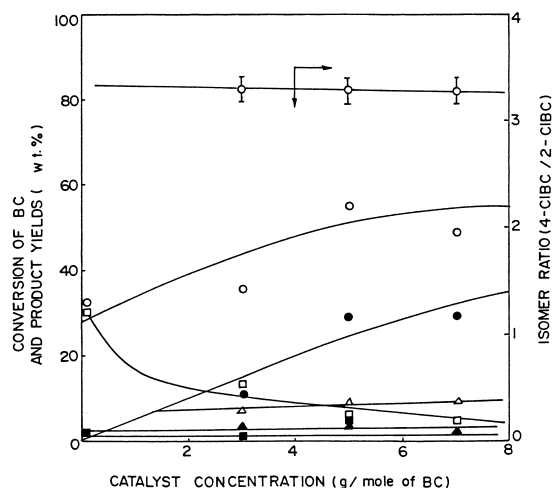


Fig. 4. Effect of catalyst (K-L) concentration on the conversion of BC (\circ), 4-CIBC/2-CIBC ratio (Φ), and product yields, 4-CIBC (\bullet), 2-CIBC (Δ), 3-CIBC (\blacktriangle), α,α -DCT (\square) and others (\blacksquare): reaction conditions: BC (mol) = 0.158, reaction temperature (K) = 353, Cl_2 flow rate (mol/h) = 0.09, reaction time (h) = 2.

the number of basic sites available for the reaction. However, the change in the isomer ratio is not observed. In the absence of catalyst mainly the side-chain chlorinated product (α,α -DCT) is noticed. These results indicate that K-L catalyzes mainly the ring chlorination of benzyl chloride.

3.7. Influence of reaction temperature

Fig. 5 shows the effect of the reaction temperature on the rate of BC conversion, product yields and the isomer ratio of 4-CIBC/2-CIBC in the chlorination of benzyl chloride. When the temperature is increased from 333 K to 388 K, both the rate of BC conversion and formation of 4-CIBC increased significantly. In addition, higher temperatures also favoured the formation of consecutive products (others), α,α -DCT, 2-CIBC and 3-CIBC (Fig. 5) and hence a decrease in the isomer ratio is noticed [15,23].

3.8. Catalyst recycling

In order to check the stability and catalytic activity of zeolite K-L in the chlorination of

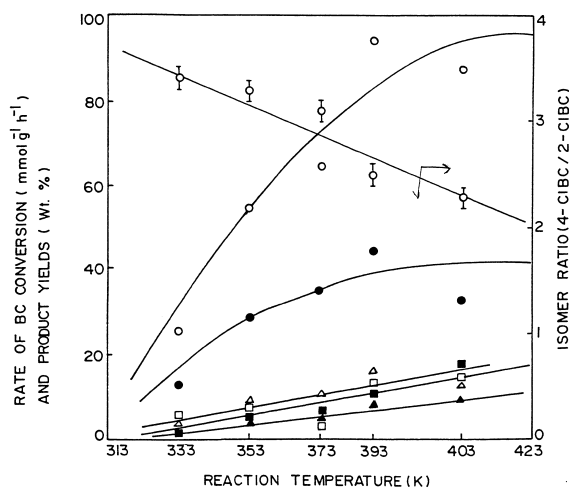


Fig. 5. Effect of reaction temperature on the rate of BC conversion (○), 4-CIBC/2-CIBC ratio (Φ) and product yields, 4-CIBC (○), 2-CIBC (Δ), 3-CIBC (\blacktriangle), α , α -DCT (\square) and others (\blacksquare): reaction conditions: catalyst (K-L) = 3.0 g/mol BC, BC (mol) = 0.158, Cl_2 flow rate (mol/h) = 0.09, reaction time (h) = 2.

benzyl chloride, three reaction cycles are carried out using the same catalyst (Table 4). After workup of the reaction mixture, the zeolite K-L was separated by filtration, washed with acetone and calcined for 16 h at 773 K in the presence of air before use in the next experiment. Thus the recovered zeolite after each reaction was characterized for its chemical composition by atomic absorption spectroscopy (AAS) and crystallinity by X-ray diffractometry (XRD). All data refers to calcined samples. AAS and XRD studies showed a downward trend in the content of aluminum and potassium and crystallinity of zeolite K-L after each recycle. The activity of zeolite K-L decreases progressively on recycling and it lost about 40% of its original activity after using three times in the chlorination of benzyl chloride. The hydrogen chloride liberated during the reaction probably promotes the extraction of aluminum and potassium to some extent from the framework positions of the zeolite K-L. Such type of extractions and decrease in crystallinity of the K-L may be attributed for the decrease in catalytic activity after each cycle. The results reported here are in good agree-

ment with the earlier reported data on the halogenation of aromatics using zeolites [15,24,31].

3.9. Mechanism

In the plausible mechanism [26–28] Cl_2 molecule is dissociated heterolytically into an electrophile (Cl^+) over zeolite catalysts which then takes part in the electrophilic substitution process resulting in the formation of ring chlorinated products [23,24]. The side-chain (α -chlorination) of benzyl chloride takes place by radical mechanism [23,25].

4. Conclusions

Zeolite K-L catalyzes the chlorination of benzyl chloride selectively to 4-chlorobenzyl chloride with Cl_2 gas as the chlorinating agent and is superior to other zeolite catalysts. Acidic H(26.1)K-L and higher concentration of K-L are favorable for better BC conversion and formation of the lower amount of α , α -DCT. 1,2-dichloroethane is found to be a good solvent and gives the highest selectivity for 4-CIBC at 353 K and lower yield for the side-chain chlorinated product (α , α -DCT). Increase in the reaction temperature in the presence of 1,2-dichloroethane (solvent) increases the rate of BC conversion and the ratio of 4-CIBC/2-CIBC. The conversion of BC increases with the increase in duration of run and reaction temperature. The increase in BC conversion does not influence the selectivity for 4-CIBC (4-CIBC/2-CIBC). Recycling of the catalyst progressively decreases the rate of BC conversion due to the extraction of small amounts of aluminum and potassium by HCl (produced in the reaction) from the catalyst. Mechanistically, the zeolite catalysts polarize the chlorine molecule and generate the electrophile (Cl^+) for the electrophilic substitution of benzyl chloride.

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