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Para-selective chlorination of benzyl chloride to 4-chlorobenzyl chloride over 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 reveals that of these catalysts zeolite H(26.1) K–L exhibits the highest rate of BC conversion (98.4 mmol g^{-1} h^{-1}) and zeolite K–L the highest selectivity of 4-chlorobenzyl chloride (4-ClBC/2-ClBC=3.7). In the absence of any catalyst or with zeolites K–X and K–Y mainly the side chain chlorination of BC to α,α-dichlorotoluene is observed. The effects of reaction time, solvents, catalyst concentration and reaction temperature are also examined. A combination of solvent and the reaction temperature not only affect the rate of BC conversion but also enhance markedly the isomer ratio of 4-ClBC/2-ClBC. 1,2-Dichloroethane is the best solvent and the isomer ratio of 4-ClBC/2-ClBC and the rate of BC conversion over zeolite K–L are enhanced from 2.21 to 7.21 and 13.2 to 51.9 mmol g^{-1} 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 reacts with BC to form the ring-chlorinated products. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: *Para*-selective chlorination; Benzyl 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-ClBC and 4-ClBC) 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-ClBC are not attractive owing to the use of expensive PCT and lower regioselectivity of iodine catalyst. In view of the

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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 [8–10]; however, their properties have not been exploited so far in the selective chlorination of BC to 4-ClBC. The aim of the present work is to enhance the yield of 4-ClBC 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-ClBC under mild reaction conditions using zeolites as catalyst and chlorine gas as the chlorinating agent. 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-ClBC/2-ClBC.

2. Experimental

2.1. Catalyst preparation

Zeolites beta and K–L samples used in this study were synthesized hydrothermally as per the literature procedures [11,12]. 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 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.

2.2. Characterization

The SiO_2/Al_2O_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 Cu K_α 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.

2.3. Catalytic reaction experiments

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 along with the appropriate amount of activated catalyst. The reaction mixture was heated to the required temperature under stirring in the presence of N_2 (20 ml min^{-1}) for 30 min. Then N_2 gas was stopped and the reaction was started by passing Cl_2 gas (0.09 mol h^{-1}). Aliquots were removed at various time intervals, filtered, neutralized with $NaHCO_3$ and analyzed by gas-chromatograph (Blue-star Model 421, equipped with a flame-ionization detector and a capillary column, 50 m$\times$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 gram of the catalyst. The yield percentage of a product represents the amount of the product calculated from the selectivity multiplied by the conversion.

Table 1
Properties of zeolites

Zeolite	SiO_2/Al_2O_3 ratio	Cation composition (%)[a]			Surface area[b] ($m^2\ g^{-1}$)	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–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

[a] Na^+ 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%.
[b] Measured by the N_2 adsorption.
[c] Values in parenthesis represent the percentage of H^+ – in K–L.

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-ClBC/2-ClBC 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-ClBC), 3-chlorobenzyl chloride (3-ClBC), 4-chlorobenzyl chloride (4-ClBC) 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 [8,10]. The most interesting feature of the reaction is that the rate of benzyl chloride conversion, product yields and the 4-ClBC/2-ClBC ratio depend on the type of zeolite used. As can be seen from Table 2, zeolites H(26.1)K–L, K–L and K–beta produce predominantly nuclear chlorinated products while in the blank experiment (without catalyst), zeolites K–Y, K–X and K–ZSM-5 exhibit mainly the side chain chlorinated product in the chlorination of benzyl chloride. 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 SiO_2/Al_2O_3 ratio than the other zeolites [13,14]. In addition, side chain chlorination of BC in the absence of any catalyst may be attributed to the photochlorination (by the free radical mechanism) of $–CH_2Cl$ group of benzyl chloride [13,15]. The results demonstrate that zeolite K–L is more active and highly selective and both the rate of benzyl chloride conversion (76.4 mmol $g^{-1}\ h^{-1}$) and the isomer ratio (4-ClBC/2-ClBC=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 mmol $g^{-1}\ h^{-1}$) and lower amount of the side chain chlorinated product (α,α-DCT) [13] 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-ClBC/2-ClBC) 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]. In addition, it was suggested [8,10] 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 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 zeolites resulting in steric hindrance at the *ortho*-position and activation of the *para*-position by electrostatic influences in the zeolite catalysts.

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

Table 2
Chlorination of benzyl chloride[a]

Catalyst	Reaction time (h)	Conversion of BC (wt%)	Rate of BC conversion[b]	Product yields (wt%)[c]					4-/2-[d] Ratio
				A	B	C	D	E	
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
None	1	15.1	–	–	–	–	15.1	–	–
	3	41.7	–	–	1.3	0.2	40.2	–	–
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

[a]Reaction Conditions: catalyst (g mol^{-1} BC)=3; reaction temperature (K)=353; BC (mol)=0.158; Cl_2 flow (mol h^{-1})=0.09; reaction time (h)=3.
[b]Rate of BC conversion in mmol g^{-1} h^{-1} is expressed as amount of BC converted/weight of the catalyst×reaction time (h).
[c]A: 2-chlorobenzyl chloride; B: 3-chlorobenzyl chloride; C: 4-chlorobenzyl chloride; D: α,α-dichlorotoluene; E: di- and trichlorobenzyl chlorides.
[d]Isomer ratio of 4-ClBC/2-ClBC.
[e]See footnote of Table 1.

3.2. Influence of duration of the run

The influence of duration of the 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. 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. K–ZSM-5 performed similarly to K–beta up to 1 h of reaction time. 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. 4-ClBC/3-ClBC ratio versus conversion

In Fig. 1, the isomer ratio of 4-ClBC/2-ClBC 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-ClBC/2-ClBC=3.7) than the other catalysts and the ratio of 4-ClBC/2-ClBC does not change with the increase in BC conversion and it remains roughly almost constant over all catalysts. The selectivity of K–beta (4-ClBC/2-ClBC=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.

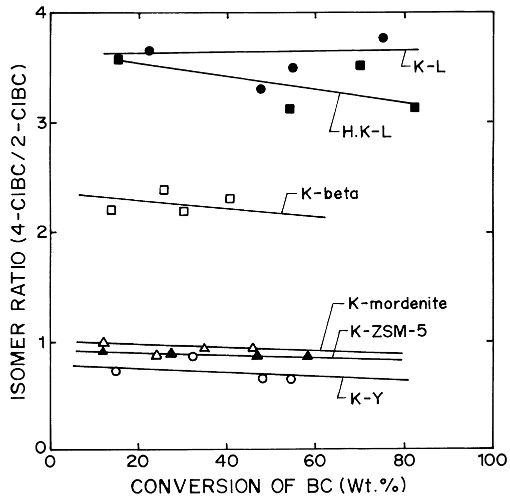

Fig. 1. 4-ClBC/2-ClBC isomer ratio versus conversion of BC over various catalysts: reaction conditions as in Fig. 1.

These results confirm that zeolite K–L plays a vital role in determining the isomer ratio of 4-ClBC/2-ClBC in the chlorination of BC. These results are in close agreement with the earlier reported data in the chlorination of toluene [14].

3.4. *Influence of solvent*

The course of the liquid-phase chlorination of aromatics over zeolite catalysts is greatly affected by the type of the solvent used in the reaction [10,14]. The rate of benzyl chloride conversion (mmol g^{-1} h^{-1}), product yields and the isomer ratio of 4-ClBC/2-ClBC obtained in the chlorination of benzyl chloride using zeolite K–L in $ClCH_2CH_2Cl$, $CHCl_3$, 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-ClBC/2-ClBC) are observed in 1,2-dichloroethane. The rate of BC conversion and the 4-ClBC/2-ClBC isomer ratio at 313 K in the presence of 1,2-dichloroethane are found to be 13.2 mmol g^{-1} h^{-1} and 2.21, respectively. The use of other solvents ($CHCl_3$, CCl_4) has led to a lower selectivity for 4-ClBC 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: $ClCH_2CH_2Cl > CCl_4 > CHCl_3$.

The over all trend of the isomer ratio (4-ClBC/2-ClBC) in these solvents at 313 K is found to be in the order: $ClCH_2CH_2Cl > CCl_4 \cong CHCl_3$.

A significant enhancement in the rate of BC conversion and the 4-ClBC/2-ClBC isomer ratio is observed with an increase in the reaction temperature in the presence of all solvents. In addition, twofold increase in the 4-ClBC/2-ClBC 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-ClBC/2-ClBC increased from 13.2 to 51.9 mmol g^{-1} h^{-1} and 2.21 to 7.21, respectively. Side-chain chlorination of BC to

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]	Product yields (wt%)[d]					4-/2-[e] Ratio
				A	B	C	D	E	
1,2-DE[f]	313	13.4	13.2	1.4	0.3	3.1	6.6	2.0	2.21
1,2-DE[f]	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 sol[g]	313	14.8	48.7	3.0	0.6	8.4	2.1	0.7	2.80
No sol[g]	353	23.2	76.4	3.3	1.4	12.2	5.9	0.4	3.69

[a]Reaction conditions: catalyst=10.1 g mol^{-1} BC; BC (mol)=0.08; Cl_2 flow (mol h^{-1})=0.09; reaction time (h)=1; solvent (ml)=10.
[c,d,e]See footnotes of Table 2.
[f]1,2-DE is 1,2-dichloroethane.
[g]Reaction conditions similar as in Table 2.

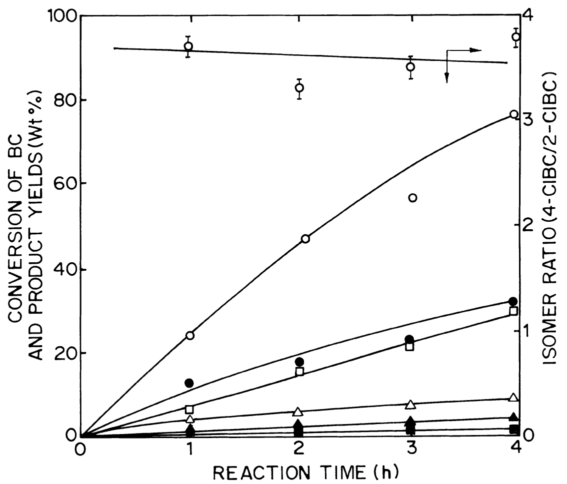

Fig. 2. Effect of reaction time on the conversion of BC (○), 4-ClBC/2-ClBC ratio (ϙ), and product yields: 4-ClBC (●); 2-ClBC (△); 3-ClBC (▲); α,α-DCT (□) and others (■); reaction conditions: catalyst (K–L)=3.0 g mol^{-1} BC, BC (mol)=0.158; reaction temperature (K)=353; Cl_2 flow rate (mol h^{-1})=0.09.

α,α-DCT to some extent is observed to be dependent on the reaction solvent. The more selective reaction in the 1,2-dichloroethane at 353 K is found to yield 1.8 wt% of α,α-DCT at 52.6 wt% conversion level of BC, whereas a higher amount of α,α-DCT, 5.9 wt%, is obtained at 23.2 wt% conversion level of BC in the neat chlorination at 353 K (Table 3). Presumably, the higher dielectric constant [16] (ionic medium) of the 1,2-dichloroethane favors the rupture of Cl–Cl bond into Cl^+ (electrophile) and hence minimizes the formation of radical (Cl$^\cdot$) which enhances the side chain chlorination of BC [13]. The higher 4-ClBC/2-ClBC isomer ratio observed in 1,2-dichloroethane in the chlorination of BC over zeolite K–L may be attributed to its higher polarity.

3.5. Influence of reaction time using zeolite K–L

A typical reaction course according to the time is pointed out in Fig. 2 for the transformation of BC over zeolite K–L at 353 K. The conversion of BC increased almost linearly with the reaction time. BC leads mainly to ring (4-ClBC, 2-ClBC) and side chain (α,α-DCT) chlorinated products. Trace amounts of ClBC and others (consecutive products) are also observed in the reaction. The results show that the reaction time influenced the conversion of BC, but did not affect the 4-ClBC/2-ClBC isomer ratio to a great extent.

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-ClBC/2-ClBC, the catalyst (K–L) concentration was increased from 3.0 g mol^{-1} of BC to 5.0 g mol^{-1} of BC. The conversion of BC increased and the formation of α,α-DCT decreased when 5.0 g catalyst per mole of BC is used in 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

The effect of the reaction temperature is studied on the rate of BC conversion, product yields and the isomer ratio of 4-ClBC/2-ClBC in the chlorination of benzyl chloride. The results are depicted in Fig. 3.

When the temperature is increased from 333 to 388 K, both the rate of BC conversion and formation

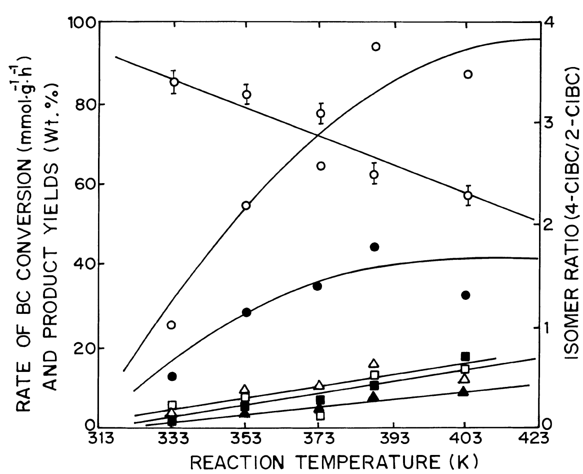

Fig. 3. Effect of reaction temperature on the rate of BC conversion (○), 4-ClBC/2-ClBC ratio (ϙ), and product yields: 4-ClBC (●); 2-ClBC (△); 3-ClBC (▲); α,α-DCT (□); and others (■); reaction conditions: catalyst (K–L)=3.0 g mol^{-1} BC; BC (mol)=0.158; Cl_2 flow rate (mol h^{-1})=0.09; reaction time (h)=2.

Table 4
Catalyst recycling[a]

Run	SiO_2/Al_2O_3 ratio	Degree of K^+- in K–L (%)	Conversion of BC (wt%)	Rate[b] of BC conversion	Product yields (wt%)					4-/2- ratio	Crystallinity of K–L (%)
					A	B	C	D	E		
0	6.82	98.6	59.8	59.0	9.5	3.7	30.1	12.7	3.9	3.2	100
1	6.97	96.7	53.0	52.3	8.1	3.5	32.2	7.1	1.7	4.0	89
2	7.09	95.0	44.8	44.2	7.0	2.8	20.1	13.5	1.4	2.9	64.7
3	7.21	93.2	35.5	35.1	4.2	1.3	8.2	20.8	1.1	2.0	46.9

[a]Reaction conditions: catalyst (g mol^{-1} BC)=5; reaction temperature (K)=353; BC (mol)=0.237; Cl_2 flow (mol h^{-1})=0.09; reaction time (h)=2.
[b,c,d]See footnotes of Table 2.

of 4-ClBC increased from 25.0 to 93.3 mmol g^{-1} h^{-1} and 13.3 to 44.8 wt%, respectively. In addition, the formation of consecutive products (others), α,α-DCT, 2-ClBC and 3-ClBC is also favored rapidly at higher temperatures (Fig. 3) and hence a decrease in the isomer ratio is noticed [10,13].

3.8. *Catalyst recycling*

In order to check the stability and catalytic activity of zeolite K–L in the chlorination of benzyl chloride, three reaction cycles are carried out using the same catalyst. The results are presented in 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 refer 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 a 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 agreement with the earlier reported data on the halogenation of aromatics using zeolite catalysts [14].

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-ClBC 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-ClBC/2-ClBC. The conversion of BC increases with the increase in duration of run and reaction temperature. The selectivity for 4-ClBC (4-ClBC/2-ClBC) is found not to be influenced by the increase in BC conversion. 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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