Selective preparation of 4,4′-dichlorodiphenylmethane over zeolite K-L catalyst using sulfuryl chloride

S.M. Kale, A.P. Singh*

Catalysis Division, National Chemical Laboratory, Pune 411 008, India

Abstract

The liquid phase chlorination of diphenylmethane (DPM) to 4,4′-dichlorodiphenylmethane (4,4′-DCDPM) is investigated at 333 K, under atmospheric pressure over a number of zeolite catalysts using sulfuryl chloride (SO_2Cl_2) as the chlorinating agent. The results obtained are compared with those over the conventional Lewis acid catalyst, $AlCl_3$ as well as without any catalyst. Zeolite K-L is found to be highly active and selective catalyst for the conversion of DPM to 4,4′-DCDPM. The conversion of DPM, rate of DPM conversion and the selectivity (4,4′-DCDPM/2,4′-DCDPM isomer ratio) over zeolite K-L after 1 h of reaction time are found to be 96.8 wt.%, 19.1 mmol g^{-1} h^{-1} and 7.4, respectively. The influence of solvent, catalyst concentration, reaction temperature, DPM/SO_2Cl_2 molar ratio, recycle of zeolite K-L, etc. are also examined. 1,2-Dichloroethane is the best solvent and gives the highest selectivity for 4,4′-DCDPM (4,4′-DCDPM/2,4′-DCDPM isomer ratio = 9.7) with zeolite K-L at 353 K after 1 h of reaction time. The formation of 4,4′-DCDPM is favoured by increase in catalyst concentration, reaction temperature and higher concentration of SO_2Cl_2 (lower DPM/SO_2Cl_2 molar ratio). In all these cases, the yield of 4,4′-DCDPM increases with a decrease in the yield of 4-CDPM which suggests that the formation of 4,4′-DCDPM takes place by the consecutive reaction of 4-CDPM. Higher SiO_2/Al_2O_3 ratio (obtained by HCl treatment) of zeolite K-L decreases the conversion of DPM. A noticeable decrease in the activity and selectivity of zeolite K-L is observed on recycling, probably due to reduced crystallinity as well as extraction of small amounts of Al^{+3} and K^+ ions by the HCl, generated in the reaction. Mechanistically, SO_2Cl_2 is first decomposed into SO_2 and Cl_2 the latter being polarized by the zeolite catalyst to an electrophile (Cl^+) which then attacks the DPM and subsequently produce the monochlorodiphenylmethane (MCDPM). The MCDPM further is attacked by the electrophile (Cl^+) and result in the formation of DCDPM. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 4,4′-Dichlorodiphenylmethane; Diphenylmethane chlorination; Zeolite K-L

1. Introduction

Ring chlorinated dichlorodiphenylmethane (DCD-PM) is useful in the preparation of agricultural and pharmaceutical chemicals or as a plasticizer for vinyl resin [1]. Traditionally, it is known that, on chlorinating diphenylmethane (DPM) with molecular chlorine, methylene group chlorinated compounds are formed. When DPM is chlorinated in the presence of azobisisobutyronitrile in CCl_4 solvent, then 66–67% α-chlorodiphenylmethane and 32–33% α,α-dichlorodiphenylmethane (α,α-DCDPM) are obtained [2]. DPM in the presence of PCl_5 with chloride gas gives only the side-chain chlorinated product [3]. Further-

* Corresponding author. Tel.: +91-21-2331453;
fax: +91-20-5893761.
E-mail address: apsingh@cata.ncl.res.in (A.P. Singh).

more, DPM when chlorinated in the presence of FeCl$_3$ as catalyst in CCl$_4$, gives monochlorodiphenylmethane (MCDPM) with a low yield and selectivity for the *para*-product [4]. In another method, DPM in the presence of CCl$_4$, azobisisobutyronitrile and ammonium molybdate at 60 °C gives MCDPM with molecular chlorine [5]. Thus, these methods are not suitable for the preparation of 4,4′-DCDPM. Also the homogeneous Lewis acid catalysts pose many problems in the chlorination reaction like formation of polychlorinated products, lower regioselectivity, difficulty of separation of the catalyst from the final product and the use of the stoichiometric amount of the catalyst. The use of heterogeneous catalyst, on the other hand, offers several advantages compared to their homogeneous counterparts, e.g. ease of recovery, enhanced selectivity and stability and recycling of the catalyst. Zeolite based catalysts are effective in meeting current industrial processing objectives and more stringent environment pollution limits which require the development of new more active and selective catalysts. Zeolites are well defined microporous crystalline materials and have been investigated extensively and applied as solid catalysts in the field of petrochemistry [6,7]. However, relatively few reports are available on the selective chlorination of aromatics using zeolite catalysts [8–25]. In addition, the chlorination of diphenylmethane in the presence of zeolite catalysts is limited to patents [26,27]. The main purpose of this study, therefore, is to enhance the selectivity for 4,4′-dichlorodiphenylmethane in the liquid phase chlorination of diphenylmethane with sulfuryl chloride (SO$_2$Cl$_2$) as the chlorinating agent using zeolite K-L as the catalyst under mild reaction conditions. Sulfuryl chloride, though a milder reagent than molecular chlorine, is more easily metered and handled in batch reaction studies, by virtue of its being a liquid.

The present paper describes the use of various catalysts in the selective chlorination of diphenylmethane with sulfuryl chloride and also compares their activity with the conventional catalyst, AlCl$_3$. The effect of solvent, catalyst concentration, reaction temperature, DPM to SO$_2$Cl$_2$ molar ratio, catalyst recycling, etc. is also investigated on the conversion of DPM, product yields, DCDPM/MCDPM ratio and the selectivity for 4,4′-DCDPM (4,4′-DCDPM/2,4′-DCDPM isomer ratio).

2. Experimental

Zeolite ZSM-5, beta and K-L samples used in this study were synthesized hydro-thermally as per the literature procedures [28–30]. The zeolite thus formed was washed with deionized water, dried and calcined at 773 K for 16 h in the presence of air. The K-forms of these zeolites were prepared by the conventional ion-exchange method, in which the zeolites were treated thrice in aqueous 1 M KNO$_3$ solution (10 ml for 1 g catalyst), at 353 K for 8 h with stirring, washed with deionized water, filtered and dried at 383 K for 2 h. Zeolite H.K-L was prepared from K-L, first by NH$_4^+$ exchange by 1 M NH$_4$NO$_3$ solution (three exchanges) followed by calcination at 773 K for 12 h. Various dealuminated K-L zeolites were prepared by treating fresh zeolite K-L (10 g each) with 100 ml aliquots of 0.05, 0.1, 0.3, 0.5, 0.7 M aqueous solutions of HCl at room temperature. The dealuminated zeolites thus obtained were further treated with 1 M KNO$_3$ to get their K-form. Laporte Inorganics, Cheshire, UK supplied zeolites Na-X, Na-Y and H-mordenite. These zeolites were converted to their K-forms following the above ion exchange procedure.

The SiO$_2$/Al$_2$O$_3$ ratio and the degree of ion exchange of these zeolites were determined by a combination of wet and atomic absorption methods (Hitachi 800). X-ray diffraction (XRD) was carried out on a Rigaku D-Max/111-VC model using Cu Kα radiation for determining the crystallinity and phase purity of the zeolite samples. No evidence of change in structure or crystallinity of K-L samples was obtained after treatment with NH$_4$NO$_3$ or KNO$_3$. The surface area of the catalysts was measured by the N$_2$ BET method. The crystal size and morphology of these catalysts were estimated by scanning electron microscope (Shimadzu, Model 2101PC). All the catalysts were activated at 523 K for 2 h prior to the reaction.

All the chemicals employed in this study were of high purity. Sulfuryl chloride was freshly distilled to a clear fraction (bp 69.5° C) before each reaction. A typical batch reaction procedure was as followed. A sample of activated catalyst (0.3 g), DPM (0.006 mol), sulfuryl chloride (0.012 mol) and 1,2-dichloroethane (EDC) were taken in a mechanically stirred, closed, 50 ml glass reactor fitted with a reflux condenser, a thermometer and a septum for withdrawing samples,

placed in a thermostat at the required reaction temperature. The samples were taken periodically, degassed thoroughly, neutralized by $NaHCO_3$ and analyzed by gas-chromatograph (HPGC 6890) equipped with a capillary column ($50 m \times 200 \mu m \times 0.2 \mu m$) with phenyl methoxy silicone gum. Product identification was done with reference to standard samples and GCMS (Shimadzu, QP 2000A).

Conversion is defined as the percentage of DPM transformed. The rate of DPM conversion ($mmol\,g^{-1}\,h^{-1}$) is calculated as the amount of DPM (mmol) converted per h per g of the catalyst. The yield percentage of product represents the amount of the product calculated from selectivity multiplied by the conversion and divided by 100.

3. Results and discussion

3.1. Influence of various catalysts

X-ray diffraction studies indicate high crystallinity and absence of any other phases in all the samples. XRD examination also gave no evidence of structure change of the zeolite sample after the cation exchange. The scanning electron micrographs reveals well-defined materials without any occluded material in the zeolites. The main properties of the zeolites are summarized in Table 1.

Table 2 compares the conversion of DPM (wt.%), rate of DPM conversion ($mmol\,g^{-1}\,h^{-1}$), product yields (wt.%), DCDPM/MCDPM ratio and the selectivity for 4,4′-dichlorodiphenylmethane (4,4′-DCDPM/ 2,4′-DCDPM isomer ratio) over various catalysts such as K-X, K-Y, K-L, K-ZSM-5, K-beta, K-mordenite, H.K-L and also the Lewis acid catalyst, $AlCl_3$ and without any catalyst (blank), in the chlorination of diphenylmethane with sulfuryl chloride at 333 K under identical reaction conditions. The reaction produces a mixture of MCDPM such as 2-chlorodiphenylmethane (2-CDPM) or (A), 3-chlorodiphenylmethane (3-CDPM) or (B) and 4-chlorodiphenylmethane (4-CDPM) or (C) and DCDPM like 2,4′-DCDPM (D), 2,2′-DCDPM (E) and 4,4′-DCDPM (F). Smaller amounts of the side-chain chlorinated product (α,α-DCDPM) (G) and polychlorinated products (others) (H) are also obtained (Scheme 1).

The MCDPM are formed by the parallel reaction by an interaction of an electrophile (Cl^+) with DPM whereas the DCDPM are obtained by the consecutive reaction of the MCDPM. It is clear from the results that zeolite K-L is highly active as well as selective in this reaction compared to the other catalysts and the conversion of DPM, the rate of DPM conversion, DCDPM/MCDPM ratio and 4,4′-DCDPM/2,4′-DCDPM ratio over zeolite K-L are found to be 96.8 wt.%, 19.2 mmol $g^{-1}\,h^{-1}$, 0.7 and 7.4, respectively, after 1 h of reaction time.

Zeolites K-X, K-Y and K-ZSM-5 and the conventional Lewis acid catalyst, $AlCl_3$, are found to be less active giving only MCDPM and higher amounts of polychlorinated products (others). Zeolites K-beta, K-mordenite and H.K-L are also less active, and give little dichlorination. Blank reaction also gives very less

Table 1
Properties of zeolites

Zeolites	SiO_2/Al_2O_3 (molar ratio)	Cation composition (wt.%)[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-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	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 Al content taken as 100%.

[b] Measured by N_2 adsorption. Value in parentheses represents the percentage of H^+ in K-L.

Table 2
Chlorination of diphenylmethane over various catalysts[a]

Catalysts	DPM conv. (wt.%)	Conv. rate (mmol g^{-1} h^{-1})[b]	Product yields (wt.%)[c]								DCDPM/ MCDPM ratio[d]	4,4'/2,4'- isomer ratio[e]
			MCDPM				DCDPM					
			A	B	C	D	E	F	G	H		
K-X	13.7	2.7	4.9	0.6	6.2	–	–	–	0.3	1.7	–	–
K-Y	20.0	4.0	5.8	0.7	8.3	–	–	–	0.1	5.1	–	–
K-L	96.8	19.1	2.5	2.0	52.7	4.6	0.8	34.0	0.1	0.1	0.7	7.4
K-ZSM-5	14.0	2.8	4.7	4.3	4.3	0.1	0.1	–	0.4	0.1	0.02	–
K-mordenite	17.7	3.5	6.9	2.0	8.1	0.8	0.2	0.2	0.3	0.3	0.07	0.3
K-beta	34.9	7.0	8.1	4.8	17.4	2.4	0.2	1.4	0.4	0.2	0.13	0.6
H.K-L	48.5	9.7	11.9	4.1	29.4	1.8	–	1.1	0.2	–	0.06	0.6
AlCl$_3$	34.1	6.8	12.2	2.0	12.3	1.6	–	–	0.7	5.3	0.06	–
Blank	12.2	2.4	–	10.5	1.7	–	–	–	–	–	–	–

[a] Reaction conditions: catalyst (g/mol of DPM) = 50.5; DPM (mol) = 0.006; SO$_2$Cl$_2$ (mol) = 0.012; 1,2-dichloroethane (ml) = 2; reaction temperature (K) = 333; reaction time (h) = 1.

[b] Rate of DPM conversion is expressed as the mmol of DPM converted per g of catalyst per h.

[c] MCDPM = monochlorodiphenylmethanes; DCDPM = Dichlorodiphenylmethanes; A = 2-chlorodiphenylmethane; B = 3-chlorodiphenylmethane; C = 4-chlorodiphenyimethane; D = 2,4'-dichlorodiphenylmethane; E = 2,2'-dichlorodiphenylmethane; F = 4,4'-dichlorodiphenylmethane; G = α,α-dichlorodiphenylmethane; H = others (polychlorinated diphenylmethanes).

[d] DC/MC ratio = dichlorodiphenylmethanes/monochlorodiphenylmethanes ratio.

[e] 4,4'/2,4' ratio = 4,4'-dichlorodiphenylmethane/2,4' dichlorodiphenylmethane ratio.

conversion with monochlorinated products. Thus, the conversion of DPM and product yields mainly depend upon the type of the catalyst used in the chlorination reaction. The results demonstrate that the conventional concept of geometry related shape-selectivity couldn't be related alone to explain the role of zeolite K-L in enhancing the *para*-selectivity. It is seen that zeolites of similar pore diameter but different structural types behave in different ways [13,17]. In addition, Wortel et al. [31] (in the bromination of halobenzenes), Botta et al. [13] (in the chlorination of biphenyl) and Singh et al. [19] (in the chlorination of toluene) suggested that factors such as size, charge and position of the cations and the electrostatic forces produced by them in the zeolite channels direct the substitution to get higher selectivity produced by them in the zeolite
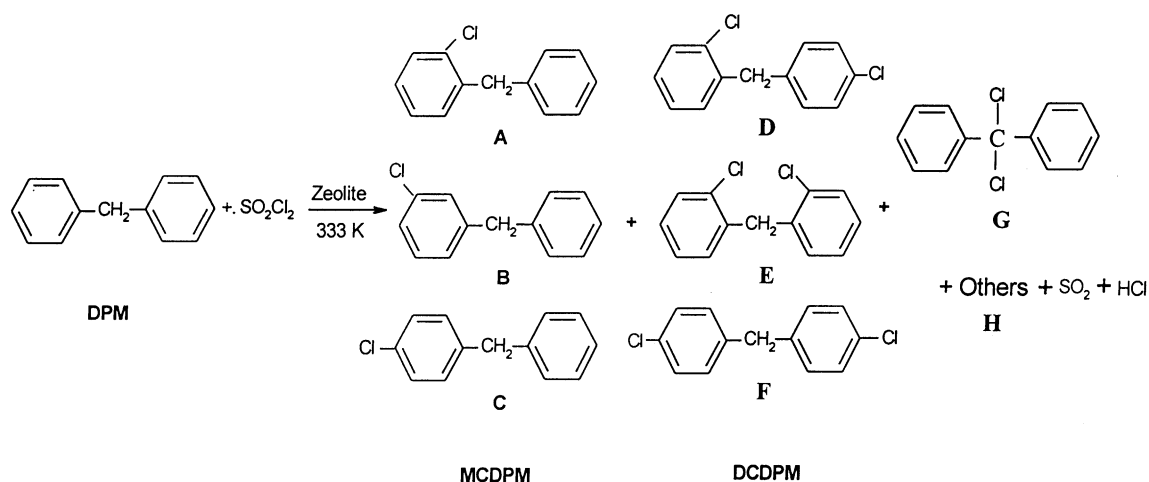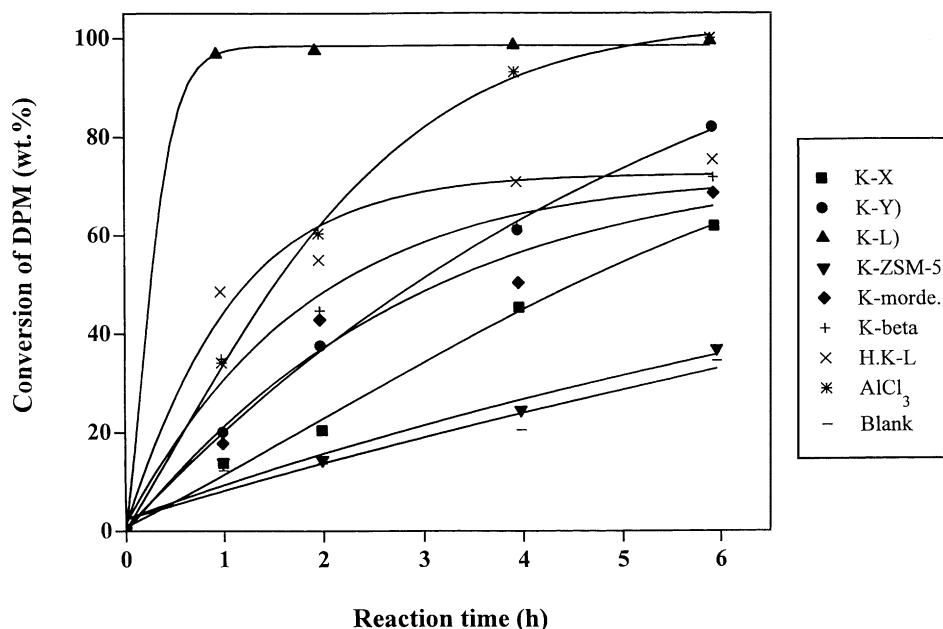

Scheme 1.

Fig. 1. Chlorination of DPM with SO_2Cl_2: effect of reaction time on the performance of various catalysts. Reaction conditions: see the footnotes to Table 2.

channels direct the substitution to get 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 the steric hindrance at the *ortho*-position and activation of the *para*-position by the electrostatic influences in the zeolite crystal. The combined effect of all these factors may be responsible for the selective formation of the 4,4′-DCDPM in the chlorination of diphenylmethane over zeolite K-L.

Zeolite K-L also has been found to be highly active and *para*-selective in the liquid phase chlorination of various aromatics such as toluene, *o*-xylene, 1,2-dichlorobenzene, *p*-chlorotoluene, benzyl chloride and cumene [20,22–25,33].

3.2. Duration of run using various catalysts

The conversion versus reaction time in the chlorination of DPM over various catalysts under similar reaction conditions is given in Fig. 1. The conversion of DPM increases over all the catalysts with

the progress of the reaction. However, zeolite K-L is highly active giving 96.8 wt.% conversion of DPM after 1 h which increased to 99.4 wt.% after 6 h of reaction time. Thus, the reaction is very fast in the presence of zeolite K-L. The conversion of DPM over the Lewis acid catalyst, $AlCl_3$ is found to be lower initially but increased slowly with time giving 100 wt.% conversion after 5 h. Based on the conversion of DPM after 6 h of reaction time, the trend in the activities of the catalysts studied is as follows:

$$AlCl_3 > \text{K-L} > \text{K-Y} > \text{H.K-L} > \text{K-mordenite}$$
$$> \text{K-X} > \text{K-ZSM-5} > \text{Blank}$$
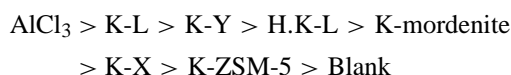
3.3. Effect of reaction time using zeolite K-L

The performance of zeolite K-L catalyst at 333 K in terms of DPM conversion (wt.%), product yields (wt.%), DCDPM/MCDPM and 4,4′-DCDPM/2,4′-DCDPM ratios as a function of time on stream is presented in Fig. 2. The conversion of DPM and product yields increase with the duration of the run. The concentration of DCDPM increases with reac-
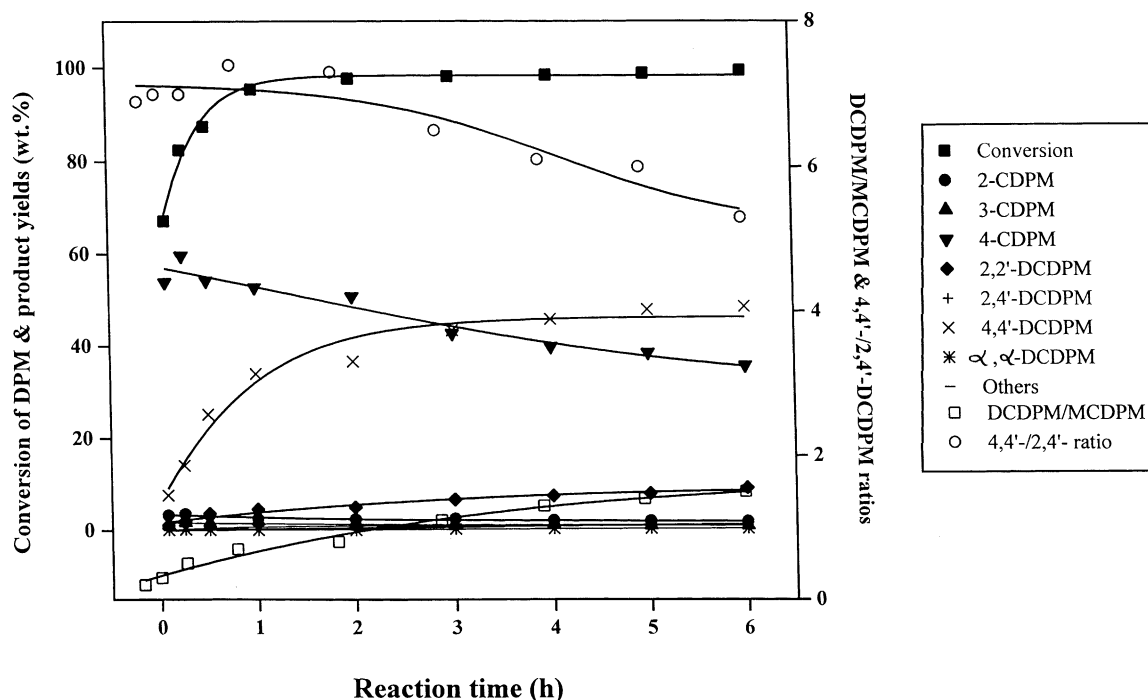
Fig. 2. Effect of reaction time on the conversion of DPM (wt.%), product yields (wt.%), DCDPM/MCDPM and 4,4′-DCDPM/2,4′-DCDPM ratios over zeolite K-L. Reaction conditions: see the footnotes to Table 2.

tion time at the expense of MCDPM and hence the DCDPM/MCDPM ratio increases with time. It is interesting to note that the yield of 4-CDPM decreases and simultaneously the yield of 4,4′-DCDPM increases with the time which suggests that the formation of 4,4′-DCDPM takes place by the consecutive reaction of 4-CDPM. The level of DPM conversion (wt.%) and the yield of 4,4′-dichlorodiphenylmethane (wt.%) are found to be 99.4 and 48.5 wt.%, respectively, after 6 h of reaction time. The selectivity for 4,4′-DCDPM (4,4′-DCDPM/2,4′-DCDPM ratio) shows a slight decrease with time on stream. The polychlorinated products (others) are found to increase with time due to the increased conversion of DPM. The side-chain chlorinated product (α,α-DCDPM) remains almost constant throughout the reaction.

3.4. Influence of solvent

Table 3 presents the conversion of DPM (wt.%), rate of DPM conversion (mmol g^{-1} h^{-1}), prod-

uct yields (wt.%), DCDPM/MCDPM as well as 4,4′-DCDPM/2,4′-DCDPM ratios obtained in the chlorination of DPM using zeolite K-L in the presence of dichloromethane (CH$_2$Cl$_2$), 1,2-dichloroethane (EDC), 1,1,1-trichloroethane (Cl$_3$CCH$_3$) and chloroform (CHCl$_3$). The nature of the reaction medium (solvent) plays an important role in the course of the liquid phase chlorination of aromatics over zeolite catalysts [9,13,20,31]. Among the solvents used, the highest activity (rate of DPM conversion) is observed in CH$_2$Cl$_2$ whereas the highest selectivity (4,4′-DCDPM/2,4′-DCDPM ratio) is obtained in EDC at 313 K. The other solvents led to a lower activity as well as selectivity under similar reaction conditions at 313 K. Thus, the activity of K-L using these solvents can be arranged in the decreasing order of their activity at 313 K as follows:

$$CH_2Cl_2 > Cl_3CCH_3 > EDC > CHCl_3$$

The overall trend of the isomer ratio over these solvents at 313 K is found to be as follows:

Table 3
Solvent effect[a]

Solvent	React temp. (K)	DPM conv. (wt.%)	Conv. rate (mmol g^{-1} h^{-1})[b]	Product yields (wt.%)[c]								DCDPM/ MCDPM ratio[d]	4,4′-/2,4′- isomer ratio[e]
				MCDPM				DCDPM					
				A	B	C	D	E	F	G	H		
EDC[f]	313	67.4	13.4	3.2	0.7	50.8	1.5	0.3	8.3	0.3	2.3	0.2	5.5
	353	98.1	19.4	1.9	0.8	44.3	4.6	1.3	44.4	0.4	0.4	1.1	9.7
CHCl$_3$	313	50.2	9.9	7.1	2.8	33.8	2.3	0.3	3.1	0.2	0.6	–	–
	333	50.4	10.0	15.7	3.9	25.9	2.5	–	1.0	0.9	0.7	0.1	0.3
CH$_3$CCl$_3$[f]	313	72.3	14.3	7.5	1.6	49.5	3.6	0.6	7.9	0.4	1.3	0.1	1.3
	345	69.8	13.8	10.7	1.4	46.4	3.7	0.5	6.3	0.4	0.4	0.1	0.4
CH$_2$Cl$_2$	313	75.8	15.0	4.1	1.6	55.3	3.2	0.4	10.7	–	–	0.2	2.2
												0.2	3.3

[a] Reaction conditions: catalyst (g/mol of DPM) = 50.5; DPM (mol) = 0.006; SO$_2$Cl$_2$ (mol) = 0.012; solvent (ml) = 2; reaction time (h) = 1.

[b] Rate of DPM conversion is expressed as the mmol of DPM converted per g of catalyst per h.

[c] MCDPM = monochlorodiphenylmethanes; DCDPM = dichlorodiphenylmethanes; A = 2-chlorodiphenylmethane; B = 3-chlorodiphenylmethane; C = 4-chlorodiphenyimethane; D = 2,4′-dichlorodiphenylmethane; E = 2,2′-dichlorodiphenylmethane; F = 4,4′-dichlorodiphenylmethane; G = α,α-dichlorodiphenylmethane; H = others (polychlorinated diphenylmethanes).

[d] DC/MC ratio = dichlorodiphenylmethanes/monochlorodiphenylmethanes ratio.

[e] 4,4′/2,4′ ratio = 4,4′-dichlorodiphenylmethane/2,4′-dichlorodiphenylmethane ratio.

[f] EDC = 1,2-dichloroethane; CH$_3$CCl$_3$ = 1,1,1-trichloroethane.

EDC > CH$_2$Cl$_2$ > Cl$_3$CCH$_3$ > CHCl$_3$

The rate of DPM conversion has increased markedly on increasing the reaction temperature to the respective reflux temperatures in case of all the solvents except CHCl$_3$. Thus, EDC is found to be best solvent and the conversion of DPM (wt.%) and the 4,4′-DCDPM/2,4′-DCDPM isomer ratio obtained are 98.1 wt.% and 9.7, respectively, with a DCDPM/MCDPM ratio of 1.1, at 353 K after 1 h of reaction time. The other solvents give less selectivity at higher temperatures as compared to EDC.

Presumably, the higher dielectric constant (ionic medium) of EDC favours the rupture of the Cl–Cl bond and formation of the electrophile (Cl$^+$) [32] which results in the formation of higher amounts of MCDPM and DCDPM. In addition, higher polarity of EDC enhances the 4,4′-DCDPM/2,4′-DCDPM isomer ratio. Furthermore, others [13,14] have suggested that solvents may influence the activation of the reactants or affect the adsorption and diffusion processes in the zeolite channels which may enhance the *para*-selectivity.

3.5. Influence of catalyst concentration

Fig. 3 shows the effect of concentration of zeolite K-L in the range of 0 to 117.8 g/mol of DPM on the conversion of DPM, product yields, DCDPM/MCDPM and 4,4′-DCDPM/2,4′-DCDPM ratios at 333 K for 0.083 h (5 min) of reaction time in the chlorination of DPM with SO$_2$Cl$_2$. Only MCDPM is formed with a very low conversion of DPM when no catalyst is used. The conversion of DPM increased from 30.4 to 98.6 wt.% when the catalyst loading is increased from 16.8 to 117.8 g/mol of DPM, respectively. Also, the yield of 4,4′-DCDPM increases with a decrease in the 4-CDPM yield as the concentration of catalyst K-L is increased. Thus, 47.1 wt.% 4,4′-DCDPM is obtained at 98.6 wt.% conversion level of DPM after 0.083 h of reaction time at the catalyst concentration of 117.8 g/mol of DPM.

The DCDPM/MCDPM as well as 4,4′-DCDPM/2,4′-DCDPM ratios also increase with an increase in the catalyst concentration.
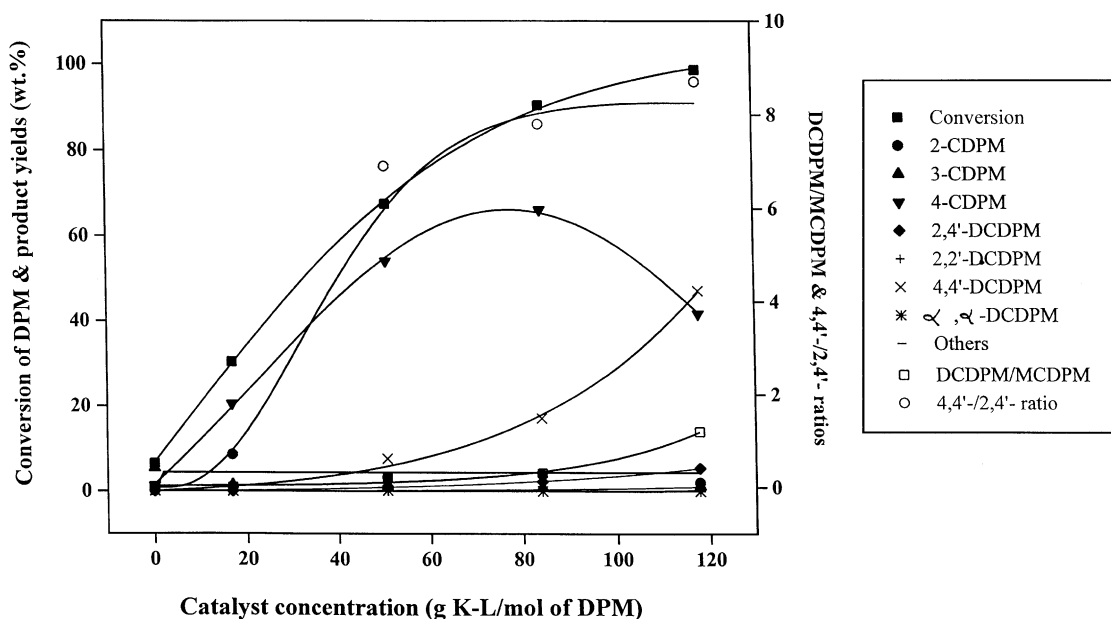
Fig. 3. Effect of catalyst (K-L) concentration on the conversion of DPM (wt.%), product yields (wt.%), DCDPM/MCDPM and 4,4′-DCDPM/2,4′-DCDPM ratios. Reaction conditions: DPM (mol) = 0.006; SO_2Cl_2 (mol) = 0.012; EDC (ml) = 2; reaction temperature (K) = 333; reaction time (h) = 0.083.
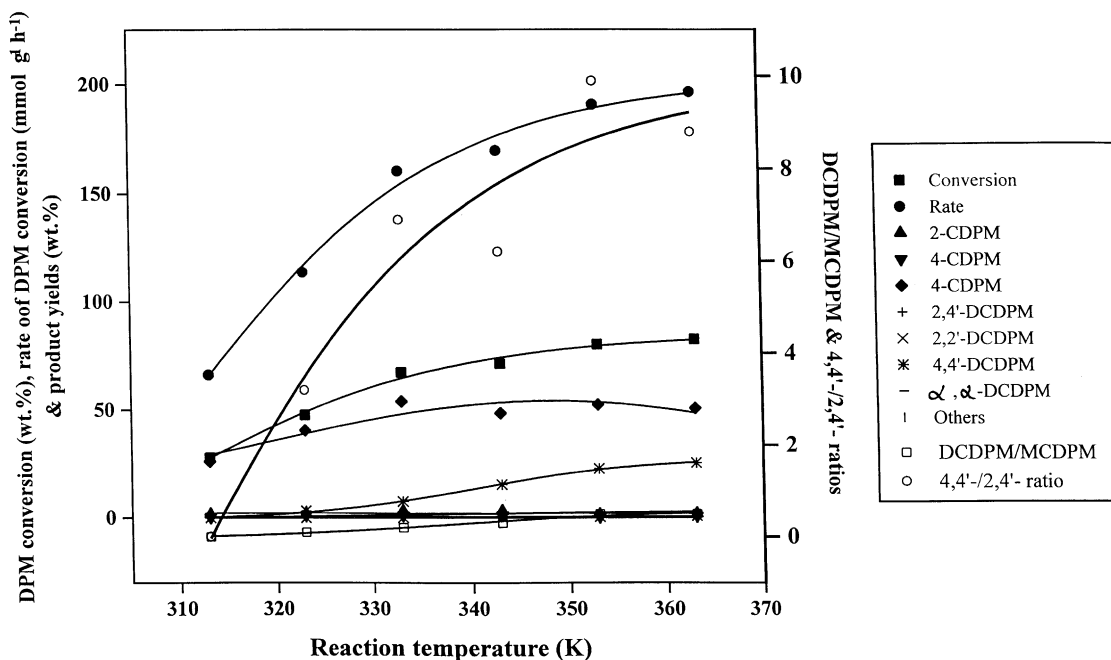

Fig. 4. Effect of reaction temperature on the conversion of DPM (wt.%), rate of DPM conversion (mmol g^{-1} h^{-1}), product yields (wt.%), DCDPM/MCDPM and 4,4′-DCDPM/2,4′-DCDPM ratios over zeolite K-L. Reaction conditions: catalyst (K-L) (g/molofDPM) = 50.5; DPM (mol) = 0.006; SO_2Cl_2 (mol) = 0.012; reaction time (h) = 0.083.

Table 4
Influence of HCl-treated zeolite K-L on the rate of DPM conversion[a]

Catalyst	SiO$_2$/Al$_2$O$_3$ molar ratio	Degree of K$^+$-exchange (%)	DPM conversion (wt.%)	Conv. Rate (mmol g^{-1} h^{-1})[b]	Product yields (wt.%)[c]								DCDPM/ MCDPM ratio[d]	4,4'-/2,4'-isomer ratio[e]
					MCDPM				DCDPM					
					A	B	C	D	E	F	G	H		
K-L	6.82	>98	67.4	160.9	3.2	1.1	53.9	1.1	0.3	37.6	0.1	0.1	0.2	6.9
K-L (0.05)[f]	7.43	>98	66.2	156.3	3.1	0.8	53.4	1.1	0.1	7.4	0.1	0.2	0.2	6.5
K-L (0.1)[f]	8.02	>98	60.2	143.7	3.3	0.7	47.4	1.1	0.3	6.8	0.3	0.3	0.2	6.2
K-L (0.3)[f]	8.63	>98	55.2	134.0	3.2	0.6	44.7	0.8	0.2	5.0	0.3	0.4	0.1	6.3
K-L (0.5)[f]	8.73	>98	46.1	110.1	2.8	0.5	38.0	0.6	0.2	3.3	0.3	0.4	0.1	5.5
K-L (0.7)[f]	9.01	>98	44.1	105.0	2.3	0.5	37.2	0.5	0.1	2.6	0.4	0.5	0.1	5.2

[a] Reaction conditions: catalyst (g/mol of DPM) = 50.5; DPM (mol) = 0.012; SO$_2$Cl$_2$ (mol) = 0.006; 1,2-dichloroethane (ml) = 2; reaction temperature (K) = 333; reaction time (h) = 0.083.

[b] Rate of DPM conversion is expressed as the mmol of DPM converted per g of catalyst per h.

[c] MCDPM = monochlorodiphenylmethanes; DCDPM = dichlorodiphenylmethanes; A = 2-chlorodiphenylmethane; B = 3-chlorodiphenylmethane; C = 4-chlorodiphenyimethane; D = 2,4'-dichlorodiphenylmethane; E = 2,2'-dichlorodiphenylmethane; F = 4,4'-dichlorodiphenylmethane; G = α,α-dichlorodiphenylmethane; H = others (polychlorinated diphenylmethanes).

[d] DC/MC ratio = dichlorodiphenylmethanes/monochlorodiphenylmethanes ratio.

[e] 4,4'/2,4' ratio = 4,4'-dichlorodiphenylmethane/2,4'-dichlorodiphenylmethane ratio.

[f] Values in parentheses correspond to the molarity of HCl solution taken for K-L treatememt.

3.6. Influence of reaction temperature

The effect of reaction temperature on the conversion of DPM (wt.%), rate of DPM conversion (mmol $g^{-1} h^{-1}$), product yields (wt.%), DCDPM/MCDPM as well as 4,4′-DCDPM/2,4′-DCDPM ratios over zeolite K-L in the liquid phase chlorination of DPM with SO_2Cl_2 is illustrated in Fig. 4. As expected, the rate of DPM conversion increases from 66.3 to 196.6 mmol $g^{-1} h^{-1}$ when the reaction temperature is increased from 313 to 363 K, respectively, after 0.083 h (5 min) of reaction time. At lower temperature (313 K) no DCDPM is detected. The DCDPM/MCDPM as well as the 4,4′-DCDPM/2,4′-DCDPM ratios increase with an increase in the reaction temperature.

The formation of 4,4′-DCDPM is favoured at higher temperature. The yield of 4-CDPM decreases thus increasing the required product (4,4′-DCDPM) with an increase in the reaction temperature. Thus, 25.5 wt.% 4,4′-DCDPM is obtained at 82.7 wt.% conversion level of DPM after 0.083 h of reaction time at 363 K.

3.7. Influence of HCl treated K-L catalysts

The chlorination of DPM was studied with zeolite K-L with different SiO_2/Al_2O_3 ratio obtained by the treatment of parent K-L with various molar solutions of HCl (0.05–0.7 M HCl). The results are presented in Table 4. As can be seen from the results, the conversion of DPM decreases from 67.4 to 44.1 wt.% after 0.083 h (5 min) of reaction time, when the SiO_2/Al_2O_3 ratio of zeolite K-L is increased from 6.82 to 9.01, respectively. The DCDPM/MCDPM and 4,4′-DCDPM/2,4′-DCDPM ratios decrease with an increase in the framework SiO_2/Al_2O_3 ratio of zeolite K-L. The higher catalytic activity of fresh zeolite K-L compared to the treated zeolite K-L may be due to the lower SiO_2/Al_2O_3 ratio thus giving higher concentration of aluminium which in turn gives higher number of basic sites for the reaction. The low activity of 0.7 M HCl treated zeolite K-L may be attributed to a combined effect of higher SiO_2/Al_2O_3 ratio and lower crystallinity of zeolite K-L. Thus, higher numbers of basic sites as well as good crystallinity of zeolite K-L are the most important factors for the liquid phase chlorination of DPM.

3.8. Influence of DPM/SO_2Cl_2 molar ratio

The conversion of DPM, product yields, DCDPM/MCDPM as well as 4,4′-DCDPM/2,4′-DCDPM ratios obtained at different DPM/SO_2Cl_2 molar ratios are demonstrated in Table 5. The conversion of DPM and the rate of DPM conversion decrease from 73.3 to 17.2 wt.%, and 175.0 to 41.1 (mmol $g^{-1} h^{-1}$),

Table 5
Influence of DPM/SO_2Cl_2 molar ratio[a]

DPM/SO_2Cl_2 molar ratio	DPM conv. wt.%	Conv. Rate (mmol $g^{-1} h^{-1}$)[b]	Product yields, (wt.%)[c]								DCDPM/ MCDPM ratio[d]	4,4′/2,4′- isomer ratio[e]
			MCDPM				DCDPM					
			A	B	C	D	E	F	G	H		
0.33	73.3	175.0	3.1	2.1	55.2	1.5	0.3	10.5	0.1	0.5	0.2	7
0.5	67.4	160.9	3.2	1.1	53.9	1.1	0.3	7.6	0.1	0.1	0.2	6.9
1	43.4	103.6	2.3	0.8	36.7	0.5	0	2.9		0.2	0.1	5.8
2	23.7	56.6	2.8	1.2	19.7	–	–	–	–	–	–	–
3	17.3	41.3	0.6	0.2	16.5	–	–	–	–	–	–	–
5	17.2	41.1	–	–	17.2	–	–	–	–	–	–	–

[a] Reaction conditions: Catalyst (g/mol of DPM) = 50.5; DPM (mol) = 0.006; 1,2-dichloroethane (ml) = 2; reaction temperature (K) = 333; reaction time (h) = 0.083.
[b] Rate of DPM conversion is expressed as the mmol of DPM converted per g of catalyst per h.
[c] MCDPM = monochlorodiphenylmethanes; DCDPM = dichlorodiphenylmethanes; A = 2-chlorodiphenylmethane; B = 3-chlorodiphenylmethane; C = 4-chlorodiphenyimethane; D = 2,4′-dichlorodiphenylmethane; E = 2,2′-dichlorodiphenylmethane; F = 4,4′-dichlorodiphenylmethane; G = α,α-dichlorodiphenylmethane; H = others (polychlorinated diphenylmethanes).
[d] DC/MC ratio = dichlorodiphenylmethanes/monochlorodiphenylmethanes ratio.
[e] 4,4′/2,4′ ratio = 4,4′-dichlorodiphenylmethane/2,4′-dichlorodiphenylmethane ratio.

Table 6
Recycle of the catalyst K-L[a]

Run	SiO₂/Al₂O₃ molar ratio	Degree of K⁺ exchange	DPM conversion (wt.%)	Conv. rate[b] (mmol g⁻¹ h⁻¹)	Product yields (wt.%)[c]										DCDPM/ MCDPM[d] ratio	4,4'/2,4'- isomer ratio[e]	Crystallinity of K-L (%)
					MCDPM				DCDPM								
					A	B	C	D	E	F	G	H					
Fresh	6.8	>98.6	67.4	160.9	3.2	1.1	53.9	1.1	0.3	7.6	0.1	0.1	0.2	6.9	100
1	7.0	>96.7	43.8	104.6	7.9	2.7	29.2	1.6	0.1	1.5	0.2	0.6	0.1	0.9	69

[a] Reaction conditions: catalyst (g/mol of DPM) = 50.5; DPM (mol) = 0.006; SO₂Cl₂ (mol) = 0.012; 1,2-dichloroethane (ml) = 2; reaction temperature (K) = 333; reaction time (h) = 0.083.

[b] Rate of DPM conversion is expressed as the mmol of DPM converted per g of catalyst per h.

[c] MCDPM = monochlorodiphenylmethanes; DCDPM = Dichlorodiphenylmethanes; A = 2-chlorodiphenylmethane; B = 3-chlorodiphenylmethane; C = 4-chlorodiphenyimethane; D = 2,4'-dichlorodiphenylmethane; E = 2,2'-dichlorodiphenylmethane; F = 4,4'-dichlorodiphenylmethane; G = α,α-dichlorodiphenylmethane; H = others (polychlorinated diphenylmethanes).

[d] DC/MC ratio = dichlorodiphenylmethanes/monochlorodiphenylmethanes ratio.

[e] 4,4'/2,4' ratio = 4,4'-dichlorodiphenylmethane/2,4'-dichlorodiphenylmethane ratio.

respectively, when the DPM/SO$_2$Cl$_2$ molar ratio is increased from 0.33 to 5, after 0.083 h (5 min) of reaction time. The higher molar ratios of DPM/SO$_2$Cl$_2$ (DPM/SO$_2$Cl$_2$ = 2, 3 and 5) give only the formation of MCDPM with a lower conversion of DPM. The DCDPM starts appearing at the DPM/SO$_2$Cl$_2$ molar ratio of 1. Thus, 2.9 wt.% 4,4′-DCDPM is obtained at a DPM/SO$_2$Cl$_2$ molar ratio of 1 which is increased to 10.5 wt.% at a DPM/SO$_2$Cl$_2$ molar ratio of 0.33 and at 0.083 h (5 min) reaction time.

3.9. Recycle of the zeolite K-L

Table 6 gives the results of a catalyst recycling experiment using zeolite K-L in the chlorination of DPM at 333 K. After the completion of each reaction, the zeolite K-L was separated from the reaction mixture by filtration, washed with acetone and calcined in air at 773 K for 12 h. It is then characterized for the chemical composition and crystallinity. All the data refers to the calcined samples. The aluminium and potassium content as well as crystallinity of K-L samples has been found to decrease after the first recycle. It has been observed that the activity of zeolie K-L is decreased in the first recycle with a drastic decrease in the 4,4′-DCDPM/2,4′-DCDPM ratio from 6.9 to 0.9, respectively, after 0.083 h (5 min) of reaction time. The sulfur dioxide and hydrochloric acid evolve continuously during the reaction, which affects the catalyst activity. In addition, the HCl formed in the reaction extracts aluminium and to some extent potassium from the framework positions of zeolite K-L. Such type of extractions and the decrease in the crystallinity of zeolite K-L attribute to the decrease in the catalytic activity of zeolite K-L in the chlorination of DPM.

3.10. Reaction mechanism

The ring chlorination of diphenylmethane takes place by an ionic mechanism, in the presence of catalysts. Sulfuryl chloride is first decomposed thermally to sulfur dioxide and molecular chlorine (Eq. (1)). The latter in the presence of catalyst, cleaves heterolytically or is polarized and the positive halogen serves as the electrophile for the aromatic substitution (Eq. (2)).

$$SO_2Cl_2 \rightarrow SO_2 + Cl_2 \tag{1}$$

$$Cl_2 \rightarrow Cl^+ + Cl^- \tag{2}$$

$$ArH + Cl^+ \rightarrow (ArHCl)^+ \tag{3}$$

$$(ArHCl)^+ \rightarrow ArCl + H^+ \tag{4}$$

$$H^+ + Cl^- \rightarrow HCl \tag{5}$$

where Ar = DPM.

A Wheland intermediate is first formed (Eq. (3)) which then deprotonates into the reaction product (Eq. (4)). The dichlorodiphenylmethanes are formed by the consecutive reactions of the monochlorodiphenylmethanes. The side-chain chlorinated product (α,α-DCDPM) is obtained by the radical mechanism.

4. Conclusions

The 4,4′-DCDPM is formed selectively over zeolite K-L in the liquid phase chlorination of DPM with sulfuryl chloride as the chlorinating agent under mild reaction conditions. Other zeolite catalysts as well as the conventional Lewis acid catalyst, AlCl$_3$, are less selective compared to zeolie K-L. The yield of 4,4′-DCDPM increases with the duration of the run, catalyst (K-L) concentration, reaction temperature and concentration of the chlorinating agent (SO$_2$Cl$_2$). In all these cases, the 4,4′-DCDPM is obtained at the expense of the 4-CDPM, thus reducing the yield of MCDPM. 1,2-dichloroethane is found to be the best solvent and gives the highest selectivity for 4,4′-DCDPM (4,4′-DCDPM/2,4′-DCDPM isomer ratio = 9.7) at 353 K after 1 h. The increase in the SiO$_2$/Al$_2$O$_3$ molar ratio of zeolite K-L (by HCl treatment) progressively decreases the activity as well as the selectivity of the catalyst. On recycling, the conversion of DPM and 4,4′-DCDPM/2,4′-DCDPM isomer ratio decreases due to the extraction of small amount of aluminium and potassium (by HCl produced in the reaction) as well as the decrease in the crystallinity of zeolite K-L. Reaction path involves the formation of molecular chlorine by the decomposition of the sulfuryl chloride which then undergoes heterolytic dissociation into an electrophile (Cl$^+$) by the catalyst, thus giving an electrophilic aromatic substitution of the DPM ring and resulting in the formation of MCDPM and DCDPM.

Acknowledgements

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