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Selective monochlorination of naphthalene over zeolite catalysts

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The liquid phase chlorination of naphthalene with gaseous chlorine to monochloronaphthalenes in high yields using K-L zeolite as catalyst is reported. The zeolite, K-L, catalyzed chlorination of naphthalene is found to be more selective than the conventional catalyst, $FeCl_3$, catalyzed chlorination.

Keywords: chlorination; naphthalene; zeolite; monochloronaphthalenes

1. Introduction

Monochloronaphthalenes are used in dyes, fungicides, insecticides, wood preservatives and as ingredients in special cleaning agents [1]. Lewis acid catalysts ($AlCl_3$, $FeCl_3$, $SbCl_5$) have traditionally been used in the chlorination of naphthalene, producing 1-chloronaphthalene and large amounts of polychlorinated naphthalenes [2,3]. The additive chlorination of molten naphthalene with molecular chlorine in the absence of any catalyst also results in the formation of large amount of polychlorinated products [4]. The best selectivity for monochloronaphthalenes (75%) reported so far was achieved with the use of $FeCl_3$ [1]. Though zeolite catalysts are being used extensively in the field of petrochemistry, only a few reports have appeared about their potential in the halogenation of aromatic compounds [5–9]. The objective of the present work is to enhance the selectivity to monochloronaphthalenes using zeolite catalysts.

We herein report the results of the influence of different zeolite catalysts, different conversion levels of naphthalene and catalyst concentration on the selectivity to monochloro- and polychlorinated naphthalenes in the chlorination of naphthalene. The results obtained over different zeolite catalysts are compared with those obtained over conventional catalysts like $FeCl_3$ and silica gel, and in the absence of any catalyst. Chlorination of naphthalene over zeolite L has not been reported so far in the open literature.

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2. Experimental

Zeolites, K-L, Na-X and Na-Y were supplied by Laporte Inorganics, Cheshire, UK. ZSM-5 and zeolite beta were synthesized using the procedures described by Argauer et al. [10] and Wadlinger et al. [11], respectively. X-ray diffraction analysis was carried out using an X-ray diffractometer (Rigaku D/Max III VC, Japan) for confirmation of the structure and crystallinity of the samples. After calcination at 823 K, the products were refluxed three times (6 h each time) with 1 M potassium nitrate solution at 353 K, maintaining the pH of the solution between 7 and 8. The K-form of the zeolites thus obtained was filtered off, washed with water and then dried at 383 K for 2 h. The chemical compositions of the zeolites were determined using atomic absorption (Hitachi Z-800) methods. The catalyst was activated before use by heating at 433 K for 2 h.

All other chemicals and solvents were anhydrous and of high purity analytical grade and were used without further purification. The chlorination of naphthalene was carried out in a 100 ml three-necked flask connected to a condenser, a gas supply line and a septum to sample the reaction mixture. 1.63 g of the reactivated zeolite (at 433 K) and a mixture of naphthalene (0.06 mol) and solvent (30 ml) were introduced in the reaction flask. The flask was purged with N_2 and placed in an oil bath. The nitrogen gas was disconnected and chlorine gas was passed at a rate of 0.03 mol/h. The progress of chlorination was followed by taking samples of the reaction mixture at suitable intervals. Product analyses were performed with a gas-chromatograph (HP 5890 series II) using a flame ionization detector and a 50 m × 0.2 mm capillary column with methyl silicon gum. GC/MS and authentic samples were used for product identification.

3. Results and discussion

The chlorination of naphthalene was carried out using various zeolites, conventional catalysts like $FeCl_3$ and silica gel, and in the absence of any catalyst. The results are listed in table 1. Substitution of chlorine in aromatic compounds in the presence of catalysts such as $FeCl_3$ or zeolites is recognised as a heterolytic reaction [5,12,13], whereas photochemical additions to the nucleus proceed through a free radical mechanism [4,14]. In order to study the difference in selectivity for monochloronaphthalenes (MCN), the catalysts are compared at nearly similar levels of conversion and under identical conditions. 1-chloronaphthalene (1-CN), 2-chloronaphthalene (2-CN) and polychlorinated naphthalenes (PCN) are the major reaction products.

Similar products have been reported in the chlorination of naphthalene using chlorine gas and $FeCl_3$ as catalyst [1]. Various zeolites were screened to get higher selectivity for MCN. During chlorination, the most reactive α-position of naphthalene is attacked preferentially to yield higher amount of 1-chloronaphthalene. It is

Table 1
Chlorination of naphthalene[a]

Catalyst	SiO_2/Al_2O_3 (molar ratio)	K^+-exchange[b] in zeolite (%)	Naphthalene conversion (wt%)	Production distribution (wt%)[c]			MCN selectivity[d] (wt%)
				1-CN	2-CN	PCN	
K-ZSM-5	41.0	96.0	32.1	76.3	5.6	18.1	81.9
K-L	6.3	98.6	27.9	87.6	7.6	4.8	95.2
K-beta	32.7	85.9	31.1	87.1	7.6	5.3	94.7
K-Y	4.1	92.8	26.6	76.8	6.1	17.1	82.9
K-X	2.4	92.6	30.5	62.6	4.7	32.7	67.3
$FeCl_3$	–	–	28.1	72.1	5.4	22.5	77.5
silica gel	–	–	35.0	75.1	3.5	21.4	78.6
no catalyst	–	–	30.3	49.3	7.0	43.7	56.6

[a] Reaction conditions: catalyst = 25.4 g/mol naphthalene; reaction temperature = 80°C; naphthalene = 0.06 mol; solvent ($ClCH_2CH_2Cl$) = 30 ml; Cl_2 flow = 0.03 mol/h.

[b] K^+-exchange in zeolites (%) = 100× moles of K/moles of Al.

[c] 1-CN = 1-chloronaphthalene; 2-CN = 2-chloronaphthalene; PCN = polychlorinated naphthalenes.

[d] MCN = monochloronaphthalenes; MCN selectivity (wt%) = 100×MCN/1-CN + 2-CN + PCN.

known that the α-position of naphthalene is more reactive than the β-position [15]. The results show a strong influence of different zeolite catalysts on the MCN selectivity in the chlorination of naphthalene which increases from 67.3 to 95.2% (table 1). Among the zeolites studied, the highest selectivity for MCN (95.2%) was obtained over zeolite K-L. The MCN selectivities over $FeCl_3$, silica gel and in the absence of any catalyst were found to be 77.5, 78.6 and 56.3%, respectively. The lowest selectivity for MCN (81.9%) among zeolite catalysts (except K-X) is observed over K-ZSM-5, which may be attributed to surface reactions. In K-ZSM-5 zeolite, the 10-ring channels have a mean diameter of 0.54×0.56 and 0.51×0.55 nm. Since naphthalene, due to its large size penetrates at a slower rate into the K-ZSM-5 channels [16], the reaction is restricted to the catalyst surface. In the case of zeolite K-L, the formation of polychlorinated naphthalenes is reduced considerably, compared to the other catalysts.

On the other hand, the results obtained in the liquid phase chlorination of naphthalene (in the zeolite channel) over different zeolites cannot be interpreted in terms of geometry related shape selectivity, table 1 [17]. The size, charge, position (potassium in this case) and electrostatic forces produced by cations in the zeolite channels may also be responsible for the formation of higher amount of MCN over K-L zeolite in the chlorination of naphthalene [5,6].

It has been reported [13] that Lewis and Brønsted acid sites of zeolite catalysts polarize the chlorine molecule and produce the required positive chlorine by heterolytic dissociation which acts as the electrophile and favours the electrophilic chlorination of aromatics.

Zeolite K-X was found to be less selective for MCN (67.3%) compared to the other zeolite catalysts and even less selective than the $FeCl_3$ and silica gel. Delaude et al. [13] have reported that $O_3SiOAlO_3$ network of the zeolite undergoes homolytic opening into $O_3SiO^\cdot + O_3Al^\cdot$ which favours the formation of polychlorinated naphthalenes through radical reactions. The highest density of such centers is to be expected with aluminum rich zeolites. The catalysts, used in this study, could be arranged in the decreasing order of their MCN selectivity as follows:

$$\text{K-L} > \text{K-beta} > \text{K-Y} > \text{K-ZSM-5} > \text{silica gel} > FeCl_3 > \text{K-X} > \text{no catalyst}.$$

Fig. 1 shows the selectivities to MCN and PCN as a function of naphthalene conversion over various zeolite catalysts, $FeCl_3$, silica gel and in the absence of any catalyst. The results indicate that as the selectivity to MCN increases, the selectivity to PCN decreases proportionally. It is observed that the selectivity for MCN is not constant (except K-X) throughout the reaction: it was found to be higher at lower

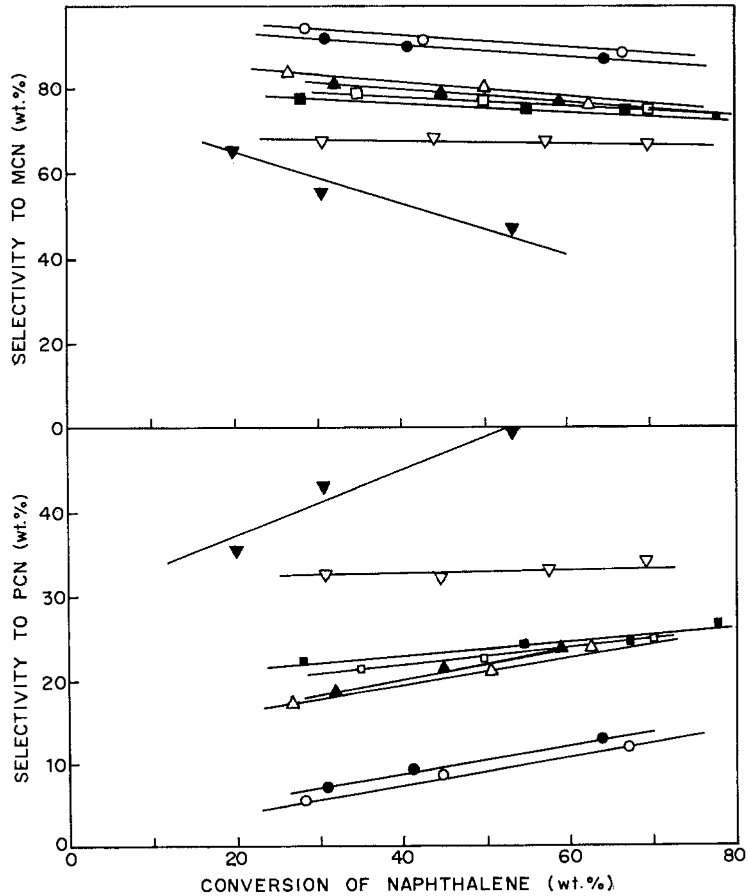

Fig. 1. Selectivity to MCN and PCN as a function of naphthalene conversion over K-L (○), K-beta (●), K-Y (△), K-ZSM-5 (▲), silica gel (□), $FeCl_3$ (■), K-X (▽), no catalyst (▼).

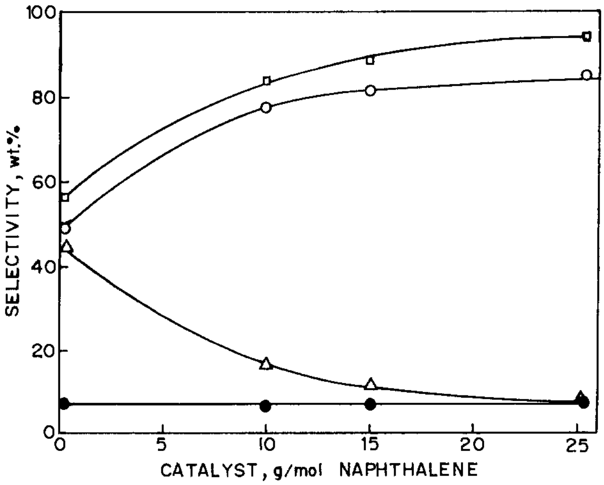

Fig. 2. Influence of zeolite K-L concentration on product distribution (wt%) at nearly similar conversion levels in the chlorination of naphthalene. Conversion of naphthalene (wt%): no catalyst, 30.3; 9.9 g catalyst/mol naphthalene 28.0, 15.0 g catalyst/mol naphthalene 29.4, 25.4 g catalyst/mol naphthalene 27.9; (○) 1-CN, (●) 2-CN, (△) PCN, (□) selectivity for MCN in product.

conversion levels and it decreases with the progress of the reaction. A larger decrease in the selectivity to MCN was observed in the uncatalyzed reaction. Zeolite K-L was found to be superior in view of its selectivity to MCN in the chlorination of naphthalene at various levels of conversion.

The amount of zeolite has a significant influence on the product distribution in the chlorination of naphthalene (fig. 2). Increasing the catalyst concentration to 10 g zeolite K-L/mol of naphthalene increases the selectivity to monochloronaphthalenes and decreases the formation of polychlorinated naphthalene. However, the concentration of 2-chloronaphthalene remains constant regardless of any amount of catalyst. Beyond the 10 g level, the selectivity to MCN in the product improved further at the expense of PCN.

4. Conclusions

The overall results show that zeolite K-L appears to be the best catalyst for the selective monochlorination of naphthalene. Zeolite K-X was found to enhance radical reactions and the formation of polychlorinated naphthalenes. An increase in catalyst (zeolite K-L) amount increases the formation of monochloronaphthalenes.

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