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Nucleophilic Substitution Reactions on Zeolites: Reaction of Chlorobenzene with Methanol on ZSM-5

Nucleophilic substitution of chlorobenzene by methanol to produce anisole was studied on HZSM-5. Chlorobenzene conversion was around 40–50% with anisole selectivity of 30–40% under the conditions used. Significant yields of methyl anisoles were observed. Thermal and catalytic cracking of chlorobenzene produced high amounts of benzene. A reaction mechanism is proposed. For comparison of activity the reaction was carried out on SK-500.

INTRODUCTION

Zeolites have been used as catalysts and adsorbents in various acid catalyzed (*1*) and non-acid catalyzed reactions (*2*). Nucleophilic substitution reactions, viz., amination, esterification, thiol formation, and etherification have been investigated on different zeolites. Holderich *et al.* (*3*) have reviewed the literature on these reactions. Production of methylamines from methanol and ammonia and of pyridine and picolines from acetaldehyde, formalin, and ammonia are some of the reactions of commercial importance in this category. Warawdekar and Rajadhyaksha have explored similar industrially relevant reactions, viz., phenol to aniline and diphenylamine from aniline on Y zeolite (*4, 5*).

Nucleophilic substitutions of chlorobenzene with ammonia and methanol have been investigated on various zeolites (*6–9*). Ren *et al.* observed chlorotoluenes for chlorobenzene reaction with methanol on H-mordenite and HZSM-5 in a pulse reactor (*8*). Preliminary studies of this reaction on SK-500 resulted in moderate yields of anisole (*9*). However, the catalyst deactivated rapidly. Anisole formation has been reported for reaction of phenol with methanol on HZSM-5 and Y zeolite (*10–12*).

In the present study the reaction of chlorobenzene with methanol was investigated on HZSM-5. The effect of some process parameters, viz., feed flow rate, molar ratio of methanol to chlorobenzene, reaction time, and temperature, on the conversion of chlorobenzene and selectivity of products was studied. For comparison, the reaction was also investigated on SK-500 under identical conditions.

EXPERIMENTAL

Catalysts and Reagents

HZSM-5 was supplied by Associated Cement Cos., India, and was synthesized in their laboratory by the reported procedure (*13*). The X-ray diffraction pattern of this sample matched with ZSM-5 of Mobil. The silica to alumina molar ratio as obtained from chemical analysis was 40. Sodium content was analyzed by flame photometer and was found to be 0.2%. The catalyst was supplied as powder without binder and contained loose agglomerates. The particle range was from 0.7 to 160 μm with an average particle size of 30 μm.

SK-500 (REHY) was supplied by Union Carbide Corp. U.S.A. as $\frac{1}{16}''$ extrudates.

Methanol (99.8%) and chlorobenzene (97.1%) were supplied by S.D. Fine Chemicals, India. The purity of these reagents was determined by GC analysis. The main impu-

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rity in chlorobenzene was dichlorobenzenes.

Apparatus and Procedure

The reaction was carried out in a stainless steel reactor (3 cm inner diameter) equipped with a preheater. Feed was introduced into the reactor by a Milton Roy dosing pump. Catalyst powder was mixed with glass beads and was placed on quartz wool supported on a steel mesh, fitted at the bottom of the reactor. Glass beads (2 mm diameter) were used to reduce pressure drop across the catalyst bed and avoid backpressure on the feed. The reactor and preheater were heated by an electric furnace. Catalyst bed temperature was monitored by a thermocouple and was controlled within ±2°C. Reactor effluents were condensed in a cold trap.

The reaction was carried out at atmospheric pressure. For each experiment 2 g of fresh HZSM-5 was heated in a flow of air (900 ml/min) at 500°C for 3 h. At the end of the pretreatment, the reactor temperature was adjusted to the desired value. Feed was pumped into the reactor by the dosing pump. Each run was extended for 1 h and liquid samples were collected at regular intervals. All the experiments were repeated; the reproducibility was ±10%.

Reaction samples had two distinct layers: an organic layer and an aqueous layer. Both the layers were analyzed on a Perkin Elmer Sigma 3B gas chromatograph with FID detector. A 2 m long, 3 mm diameter SS column packed with 10% OV-17 on Chromosorb WHP (80–100 mesh) was used for analysis. The carrier gas was nitrogen. Benzene, toluene, anisole, and methyl anisoles were identified as the main products. Minor quantities of phenol and cresols were also detected. Unreacted chlorobenzene and reaction products were detected in the organic layer while unreacted methanol and small amounts of main products were detected in the aqueous layer.

Response factors of the main products with respect to chlorobenzene were determined from GC analysis using mixtures of known concentrations of each product and chlorobenzene. The mole fraction of each product in a sample was calculated with these response factors. The selectivities of main products mentioned in the tables do not include the amounts detected in the aqueous layer.

RESULTS

Initially the effect of feed rate on conversion of chlorobenzene and product selectivities was studied at 500°C and at a methanol to chlorobenzene ratio of 1.0. The results are given in Table 1. Chlorobenzene conversion decreased with increase in feed rate. Selectivities of benzene and anisole increased and those of toluene and methyl anisoles decreased with increase in feed rate. Considering the trends in selectivities

TABLE 1

Effect of Feed Rate on Conversion of Chlorobenzene and Selectivity of Products

W/F $\left(\frac{\text{g cat-h}}{\text{g feed}}\right)$	Conversion of chlorobenzene (mol%)	Selectivity of products (mol%)				
		Benzene	Toluene	Anisole	Methyl anisoles	Others
0.093	53.2	25.2	23.0	25.8	12.3	13.7
0.080	47.7	28.5	20.8	27.6	11.1	12.0
0.069	41.5	33.6	16.3	30.9	9.8	9.4
0.055	34.1	41.9	12.5	37.0	4.0	4.6

Note. Reaction conditions: reaction temperature, 500°C; methanol to chlorobenzene molar ratio, 1.5; time of sample, 5 min; amount of catalyst, 2 g.

TABLE 2

Effect of Reaction Temperature on the Activity of HZSM-5

Reaction temperature (°C)	Conversion of chlorobenzene (mol%)	Selectivity of products (mol%)				
		Benzene	Toluene	Anisole	Methyl anisoles	Others
400	42.1	9.6	12.0	39.1	24.9	14.4
450	44.7	19.9	16.6	32.5	17.6	13.4
500	48.1	30.0	19.9	26.7	11.5	11.9

Note. Reaction conditions: W/F, 0.078 g cat-h/g feed; methanol to chlorobenzene molar ratio, 1.5; time of sample, 5 min.

of the products, all further experiments were carried out at a feed rate of 25.5 ml/h.

Variation in methanol-to-chlorobenzene molar ratio from 0.5 to 1.5 at 500°C did not affect the conversion of chlorobenzene and the product selectivities significantly. Conversion increased marginally from 46.7 to 49.2% and selectivities of benzene, toluene, anisole, and methyl anisoles were almost constant around 30.0, 20.0, 28.0, and 11.0%, respectively.

The effect of reaction temperature on conversion and selectivities is given in Table 2. With decrease in reaction temperature from 500°C to 400°C, chlorobenzene conversion decreased from 48.1% to 42.1%. Selectivities of anisole and methylanisoles increased but those of benzene and toluene decreased with decrease in temperature. Catalyst activity was better at 400°C due to slower deactivation.

Catalyst activity decreased with time due to carbonaceous residues ("coke") formation (see Table 3). The effect of time on selectivities was found to be similar to that observed by decreasing the temperature. Benzene selectivity dropped by 67% after 50 min and toluene selectivity decreased by 33%. There was a marginal decrease in the selectivity of methylanisoles during the run time. However, anisole selectivity almost doubled. The decrease in activity with time at high temperature is expected since at temperature >400°C, methanol undergoes chain reactions leading to coke formation and hence catalyst deactivation (*14, 15*).

Thermal cracking of chlorobenzene was investigated. At 500°C, chlorobenzene conversion was 14%. Benzene was the major product with 90% selectivity.

Catalytic cracking of chlorobenzene on HZSM-5 was also investigated at 500°C.

TABLE 3

Catalyst Activity Vs Time[a]

Time (min)	Conversion of chlorobenzene (mol%)	Selectivity of products (mol%)				
		Benzene	Toluene	Anisole	Methyl anisoles	Others
5	48.1 (34.3)	30.0 (36.1)	19.9 (24.6)	26.7 (23.0)	11.5 (9.1)	11.9 (7.2)
15	46.3 (16.0)	25.9 (32.3)	17.5 (7.0)	31.4 (23.3)	10.6 (9.2)	14.6 (28.2)
30	41.0 (6.9)	17.0 (27.9)	15.2 (—)	40.6 (24.7)	9.7 (8.2)	17.5 (39.2)
50	32.4 (—)	10.4	12.2	52.1	8.8	16.5

Note. Reaction conditions: reaction temperature, 500°C; W/F, 0.078 g cat-h/g feed; methanol to chlorobenzene molar ratio, 1.5.

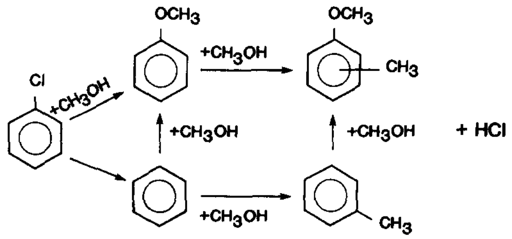
[a] Results in parentheses are for SK-500 at a reaction temperature of 450°C, other conditions being the same.

Chlorobenzene conversion was 26% and selectivity of benzene was 75%. Catalyst deactivation was negligible in the absence of methanol.

Analysis of the aqueous layer in product samples indicated the presence of HCl. Hence, the possibility of catalyst deactivation by HCl was investigated. In one experiment 1% HCl solution was passed over HZSM-5 for 30 min at 500°C and then the reaction of chlorobenzene and methanol was carried out. Alternately, 1% HCl solution was pumped along with the feed at a reaction temperature of 500°C. The activity of the catalyst and product selectivities in both the experiments were similar to those wherein no HCl was introduced. Thus, HCl does not cause catalyst deactivation.

DISCUSSION

From the results of thermal cracking of chlorobenzene, it is obvious that a small amount of benzene is present in the feed when it passes over the catalyst. In the catalytic cracking of chlorobenzene, too, benzene was the major product. Thus, benzene is the primary product in the reaction of chlorobenzene and methanol. In methanol conversion to gasoline-range hydrocarbons, Chang has postulated a reaction mechanism through CH_3^+ and CH_3O^- ions on HZSM-5 (*16, 17*). In the present case, CH_3O^- will react with chlorobenzene to produce anisole. The overall reaction scheme can be envisaged as



A similar scheme has been proposed for the reaction of phenol with methanol on HZSM-5 (*10, 11*). Additionally, benzene and toluene will be produced directly from methanol (*16, 17*).

It is interesting to note that, although chlorobenzene conversion as well as selectivities of benzene and toluene decreased significantly with time, the selectivity of anisole increased twofold and that of methyl anisoles decreased marginally (see Table 3). This observation can be explained on the basis of the nature of the acidic sites of ZSM-5. It is reported that ZSM-5 has strong, medium, and weak acidic sites (*18, 19, 20*). Cracking and alkylation reactions occur on strong and medium acidic sites. Thus, cracking of chlorobenzene and alkylation of benzene are expected to occur on strong and medium acidic sites, which deactivate fast due to coke formation (*14*). Hence, the yields and selectivities of benzene and toluene decreased with time. In contrast, anisole formation occurs on weak acid sites (*11, 21*), which deactivate very slowly. Hence, anisole yield was not affected and higher selectivity of anisole was observed. Similar increase in selectivity of anisole with time was observed by Balsama *et al.* on Y zeolite (*10*). As per the reaction scheme given above, methyl anisoles are postulated to form via alkylation of anisole or CH_3O^- addition to toluene. Since alkylation reactions will be suppressed due to coke formation, methyl anisoles' yield and selectivity will decrease with time.

Increase in selectivity of benzene with increase in temperature is expected since thermal and catalytic cracking reactions are slow at lower temperatures (less than 400°C) and the rates of these reactions increase significantly above 450°C. Thus, yield of benzene, which is the primary product of cracking of chlorobenzene, will increase with increase in temperature. A decrease in yield and selectivity of anisole with increased temperature was observed by Renaud *et al.* (*12*) in the reaction of phenol with methanol. Similar observations were made in this study.

For comparison the reaction was also studied on SK-500. At 500°C and W/F of 0.078, SK-500 deactivated rapidly and the activity was negligible after 20 min. At

450°C, deactivation was slower. The results for the reaction at 450°C are given in Table 3. Comparing the results for HZSM-5 at 450°C (see Table 2), it is evident that on SK-500 cracking and alkylation are predominant compared to nucleophilic reaction. Thus, anisole formation is lower than on HZSM-5.

CONCLUSION

(1) Reaction of chlorobenzene with methanol on HZSM-5 gives satisfactory yields of anisole. By suppressing the strong acidic sites of HZSM-5 it should be possible to produce anisole with high selectivity.

(2) On SK-500 high selectivities for benzene and toluene were observed; anisole formation was lower compared to HZSM-5. Thus, SK-500 doea not appear to be suitable for anisole production.

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