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SELECTIVE N-MONOALKYLATION OF ANILINE OVER ALKALI CATION EXCHANGED X AND Y TYPE ZEOLITES

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Potassium cation exchanged X and Y type zeolites are found to work as efficient bases in N-alkylation of aniline with an alkylating reagent in benzene. The intrinsic pore structures of X and Y zeolites are responsible for the high selectivity in N-monoalkylation of aniline.

Recently considerable attention has been given to selective organic syntheses over inorganic supports such as silica gel and alumina.[1)] We are particularly interested in well-defined crystalline aluminosilicate zeolites as inorganic supports, since various cation exchanged zeolites have been employed as acid or base catalysts and their intrinsic homogeneous cavities in the zeolite crystalline structure can discriminate the molecular shapes of reactants or products in organic reactions.[2)] Many investigations on catalytic behavior of zeolites have been undertaken mainly for the gas-phase reactions. The basic property of zeolites is considered to be derived from the $(AlO_4)^-$ moiety in the lattice.[3)] Alkali metal cation exchanged zeolites, especially when the metal has lower electron negativity, exhibit strong basicity in the gas phase. However little study has been made on the basicity of zeolites in the liquid phase, particularly in organic solvents.

On the other hand, the reaction of primary amine with an alkylating reagent in the presence of a base usually produces a mixture of secondary amine, tertiary amine, and quaternary ammonium salt. It is difficult, therefore, to obtain secondary amine selectively from primary amine in a direct manner.

$$RNH_2 \ + \ R'X \xrightarrow{\text{Base}} RR'NH \ + \ RR'_2N \ + \ RR'_3N^+X^- \ + \ HX{\cdot}Base$$

We wish to report here that alkali metal cation exchanged zeolites can work effectively as a base in organic solvents and promote the selective N-monoalkylation of aniline even though equivalent amounts of aniline and an alkylating reagent are employed.

The zeolites used, Linde 13X (abbreviated as NaX), Linde 13Y (NaY), mordenite (NaZ), and Linde 3A (3A), were all purchased. The potassium ion exchanged zeolites (KX, KY, KZ) were prepared according to the ion exchange technique: Zeolite (35-60 mesh, 5 g) was immersed in an aqueous 0.5 N KCl solution (50 ml) at 70°C for 1 h and then the aqueous solution was decanted. This procedure was repeated 10 times. Next the ion exchanged zeolite was washed with deionized water until no chloride ion was detected in the wash water, and dried at 110°C for 10 h, successively at 500°C for 12 h in air. N-Alkylation of aniline was carried out under an argon atmosphere. A mixture of aniline, an alkylating reagent, and zeolite was stirred in solvent vigorously under the conditions shown in the tables. The reaction mixture was worked up according to the following two procedures: 1) A 2 N HCl solution was added to the reaction mixture to dissolve the zeolite.[4] The resulting solution was basified with aqueous alkali and filtered. The products were extracted with dichloromethane from the filtrate and analyzed by use of GLC. 2) Water was added to the reaction mixture and the mixture was refluxed for 2 h with vigorous stirring. The solution was filtered and the organic products were extracted with dichloromethane and analyzed by means of GLC.[5] The analytical results obtained by these procedures were almost the same each other. According to the second work-up procedure, zeolite could be recovered and reused as a base in the same efficiency as obtained with the fresh zeolite.

N-Monobutylation of aniline

Table 1 shows the results of the reaction of aniline with butyl iodide in organic solvents. In the absence of a base, N-butylaniline was scarecely produced. In contrast, the addition of KX zeolites to the reaction mixture remarkably promoted the N-butylation of aniline to give a mixture of N-butylaniline and N,N-dibutylaniline in a molar ratio of 74 : 1 at a 64 % conversion of aniline.[6] As indicated in Table 1, benzene was the best solvent. More polar solvents such as N,N-dimethylformamide, acetonitrile, tetrahydrofuran, and 1,2-dimethoxyethane decreased the conversion of aniline and/or the selectivity of N-butylaniline. It is suggested that these polar solvents may be predominantly adsorbed in the zeolite cages and decrease the basicity or the effective pore size of the zeolite. X and Y zeolites were far more effective for the selective formation of N-butylaniline than Z and 3A zeolites. Probably the basicity of mordenite (KZ, NaZ) in benzene is too low to accelerate the N-butylation as suggested by the low content of the $(AlO_4)^-$ moiety in the mordenite lattice.[7] Linde 3A has smaller pore structures than KX and KY,[8] and hence aniline molecules may be hardly accessible to the basic sites in the zeolite pores and can not be promoted to react with butyl iodide. Potassium ion exchanged X and Y zeolites were usually more efficient bases than the sodium ion exchanged zeolites. This fact indicates that the potassium ion exchanged zeolites are more basic in benzene than the sodium ion exchanged zeolites. A similar discussion on the basicity of alkali cation exchanged zeolites was reported in the gas-phase decomposition of 2-propanol.[3] Usual organic or inorganic bases such as tributylamine, sodium carbonate, and potassium fluoride impregnated on Celite[9] are also applied to N-butylation of aniline. Compared with the results using X and Y zeolites, the selectivity of N-butylaniline was far low. These facts imply that the N-butylation of aniline in the presence of X or Y zeolite takes place at the basic sites in the pores of zeolite, and thus the zeolite reveals good shape selectivity of the products.

Table 1 N-Butylation of aniline with butyl iodide[a)]

Base	Solv.	Temp.	Time(h)	Conv.(%)	$Ph^{n}BuNH : Ph^{n}Bu_2N$
None	C_6H_6	refl.	23	1.4	—b)
KX (0.5 g)	C_6H_6	refl.	14	64	74 : 1
KX (0.5 g)	DMF	90°C	14	33	5.4 : 1
KX (0.5 g)	CH_3CN	refl.	14	39	3.2 : 1
KX (0.5 g)	THF	refl.	14	13	68 : 1
KX (0.5 g)	DME	refl.	14	9.7	—b)
NaX (0.5 g)	C_6H_6	refl.	14	47	82 : 1
KY (0.5 g)	C_6H_6	refl.	14	67	97 : 1
NaY (0.5 g)	C_6H_6	refl.	14	58	120 : 1
KZ (0.5 g)	C_6H_6	refl.	14	6.1	—b)
NaZ (0.5 g)	C_6H_6	refl.	14	2.1	—b)
3A (0.5 g)	C_6H_6	refl.	14	0.8	—b)
$^{n}Bu_3N$ (1.0 mmol)	C_6H_6	refl.	16	26	8.7 : 1
Na_2CO_3 (0.5 mmol)	Neat	80°C	5	57	1.3 : 1
KF-Celite(0.75 mmol)	CH_3CN	r.t.	43	41	6.2 : 1

a) Reaction conditions: $PhNH_2$ (0.5 mmol), ^{n}BuI (0.5 mmol), Solv. (3 ml).

b) Product ratio was not determined.

Table 2 N-Methylation of aniline with methyl iodide[a)]

Base	Conv.(%)	$PhMeNH : PhMe_2N$
KX (0.5 g)	36	18 : 1
3A (0.5 g)	3	39 : 1

a) Reaction conditions: $PhNH_2$ (0.5 mmol), MeI (0.5 mmol), Solv. C_6H_6 (3 ml), 30°C, 48 h.

Table 3 N-Methylation of aniline with dimethyl sulfate[a)]

Base	Conv.(%)	$PhMeNH : PhMe_2N$
None	34	2.2 : 1
KX (0.25 g)	59	4.0 : 1
KX (0.5 g)	63	12 : 1
KX (1.0 g)	57	32 : 1
NaX (0.5 g)	52	3.0 : 1
KY (0.5 g)	71	8.9 : 1
KY (1.0 g)	58	21 : 1
NaY (0.5 g)	53	2.6 : 1
Na_2CO_3 (0.5 g)	66	3.0 : 1
DBU (0.5 mmol)	2.8	—b)

a) Reaction conditions: $PhNH_2$ (0.5 mmol), Me_2SO_4 (0.25 mmol), Solv. C_6H_6 (3 ml), refl., 9 h.

b) Product ratio was not determined.

N-Monomethylation of aniline

The N-methylation of aniline with methyl iodide did not proceed well at 30°C even in the presence of zeolites (Table 2). However dimethyl sulfate was favorably employed as a methylating reagent under reflux in benzene. Both KX and KY zeolites promoted the N-methylation of aniline and gave high product selectivity of N-methylaniline in comparison with the results in the presence of sodium carbonate or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Table 3). The increase of the amount of zeolite (KX, KY) in the reaction system enhanced the product selectivity, which clearly suggests that the N-methylation of aniline occurs predominantly in the zeolite pores. The preadsorption of either aniline or dimethyl sulfate on KX zeolites gave little influence on the selectivity in N-methylation compared with the results obtained by mixing all the substrates simultaneously.

In conclusion, potassium ion exchanged X and Y type zeolites are found to work as effective bases in N-alkylation of aniline in organic solvents and the shape selective nature of the pore structure of zeolites is responsible for the higher selectivity of N-monoalkylation of aniline.

References

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2) P. B. Venuto and P. S. Landis, "Advances in Catalysis and Related Subjects," Vol. 18, P. 259, Academic Press (1968).
3) T. Yashima, H. Suzuki, and N. Hara, J. Catal., 33, 486 (1974).
4) Linde 13X (NaX, KX) and Linde 3A are soluble in 2 N HCl, but Linde 13Y (NaY, KY) and mordenite (NaZ, KZ) are insoluble in 2 N HCl.
5) As zeolites can include a small amount of organic compounds tightly in their pores, the organic compounds can not be completely recovered from zeolites only by rinsing the zeolites with organic solvents. Therefore in order to recover the products completely we must either break down the structure of zeolites with an acid or replace the organic compouds in zeolites with a polar substance such as water.
6) Quaternary ammonium salts could not be detected in N-alkylation of aniline using zeolites.
7) The SiO_2/Al_2O_3 ratio is 2-3 in X type zeolite, 3-5 in Y type zeolite, and 10 in mordenite.
8) The pore size is 10 Å in X and Y type zeolites and 3 Å in Linde 3A.
9) T. Ando and J. Yamawaki, Chem. Lett., 1979, 45.

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