

## Isomerisation of *N*-isopropylaniline and *N*-*n*-propylaniline over zeolites

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Reactions of *N*-isopropylaniline and *N*-*n*-propylaniline over Ce, H and Na forms of ZSM-5 and Y type zeolites at 200–400° have been investigated. Both the secondary amines isomerised on zeolites to produce *o*-isopropylaniline and *p*-isopropylaniline through S<sub>N</sub>1 mechanism and also dealkylated to give aniline and propene. The *ortho*-isomer is the major *C*-alkylated product. Effects of temperature and flow rate on activity and selectivity have been studied.

Rearrangement of *N*-alkylanilines to ring-alkylated anilines on heating in the presence of acid is known. The major *C*-alkylated product formed from rearrangement is the *para*-isomer. Generally hydrohalides have been used for this. Alumina, titania or tungstic oxide catalyst were used for rearrangement of *N*-methyl- and *N*-ethyl-anilines to *para*-alkylated anilines<sup>1</sup>. The vapour phase reaction of *N*-ethyl-aniline over alumina in the temperature range of 250–350° was reported<sup>2</sup>. It is also reported that ethyl group migrated intramolecularly from nitrogen to the ring. During the *ortho*-alkylation of arylamines with alkynes by Friedel-Crafts method, *N*-alkylated products are formed if the amine group is not protected<sup>3</sup>. Aniline alkylation is generally carried out in liquid phase using homogeneous catalysts<sup>4</sup>, and *N*-alkylated aniline is the major product. The vapour phase alkylation of aniline with methanol<sup>5</sup>, ethanol<sup>6</sup> and propanol<sup>7</sup> using zeolites produces *N*-alkyl and *C*-alkylanilines. Alkylation of arylamines with propene using H-Y zeolite and Al<sub>2</sub>O<sub>3</sub> catalyst produces like *ortho*- and *para*-isopropylanilines, di- and tri-alkylated anilines<sup>8</sup>. Since synthesis of *ortho*- and *para*-isopropylanilines from *N*-alkylated aniline using ion exchanged zeolites was not reported in detail, the present study was taken up.

### Results and Discussion

Reaction of *N*-*n*-propylaniline over zeolites : Rearran-

gement of *N*-*n*-propylaniline over different zeolites like Ce, H and Na forms of Y and ZSM-5 zeolites were studied. The results are listed in Table 1. *N*-*n*-Propylaniline dealkylated on zeolite to give aniline and propene. Aniline and propene reacted to form *ortho*- and *para*-isopropylanilines. The yield of *ortho*-isomer was more than that of *para*-isomer. This may be due to the proximity of the alkylating agent (propene) which is on the surface of catalyst to the *ortho*-position of the aniline.

As expected the conversion of *N*-*n*-propylaniline increased with increase in temperature and increase in acidity of catalyst rate of conversion decreased with increase in rate of flow. The selectivity towards *C*-alkylation increased with increase in contact time (decrease in flow rate) (Table 1).

Aniline was the major product at all temperatures and under all flow-rates. The *ortho*-selectivity during alkylation of aniline with propylene was reported<sup>9</sup>. *Ortho*-substitution that took place at the secondary carbon may be explained by a mechanism which requires initial dissociation of *N*-*n*-propylaniline to aniline and propene. Such a mechanism has been suggested for *ortho*-alkylation of aniline by styrene under acidic conditions<sup>10</sup>. The formation of *p*-isopropylaniline is through transalkylation of aniline with

Table 1. Reaction of *N*-*n*-propylaniline (A) and *N*-isopropylaniline (B) over zeolites

Weight of catalyst = 5 g

Catalyst	Mole % conversion		Mole % yield of products					
			Aniline		<i>o</i> -Isopropylaniline		<i>p</i> -Isopropylaniline	
	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)
Ce-Y <sup>a</sup>	48.7	92.3	35.8	52.7	9.1	28.6	3.8	11.0
H-Y <sup>a</sup>	37.3	61.4	25.5	37.5	8.5	17.8	3.3	6.1
Na-Y <sup>a</sup>	16.8	32.3	11.2	21.4	3.9	8.5	1.7	2.9
Ce-ZSM-5 <sup>a</sup>	36.3	71.0	25.5	41.9	7.9	21.3	2.9	7.8
H-ZSM-5 <sup>a</sup>	28.2	52.6	18.9	30.6	6.8	16.3	2.5	5.7
Na-ZSM-5 <sup>a</sup>	13.2	27.2	10.0	18.0	2.2	6.5	1.0	2.7
H-ZSM-5 <sup>b</sup>	21.4	38.6	15.8	26.3	4.1	8.8	1.5	3.5
H-ZSM-5 <sup>c</sup>	11.8	16.3	9.6	9.9	1.5	5.3	0.7	1.1
H-ZSM-5 <sup>d</sup>	14.6	13.6	11.6	9.6	1.9	2.9	1.1	1.1
H-ZSM-5 <sup>e</sup>	34.3	68.7	19.11	35.7	11.3	24.7	3.6	8.3

<sup>a</sup>Flow rate, 10 ml h<sup>-1</sup>; temp 30°. <sup>b</sup>Flow rate, 20 ml h<sup>-1</sup>; <sup>c</sup>Flow rate, 30 ml h<sup>-1</sup>; <sup>d</sup>Temp 200°; <sup>e</sup>Temp 400°

propene by  $SN_1$  mechanism.

*Reactions of N-isopropylaniline over zeolites* : Reactions of *N*-isopropylaniline over Ce, H and Na forms of Y and ZSM-5 zeolites were carried out in the temperature range 200–400°. The results are shown in Table 1. Aniline and propene were formed by dealkylation of *N*-isopropylaniline. Aniline reacted with propene to form *ortho*- and *para*-isopropylanilines. Yield of *ortho*-isomer was more than that of *para*-isomer in all reactions studied.

The conversion of *N*-isopropylaniline (92%) was more than that of *N*-*n*-propylaniline (48%) under identical reaction conditions. This proves that *N*-*n*-propylaniline is more stable than *N*-isopropylaniline under identical reaction parameters. Also the conversion of secondary amine increased steadily with rising temperature and the conversion increased with increase in contact time. Selectivity towards *C*-alkylation also increased with increase in contact time (Table 1).

### Experimental

*N*-Isopropylaniline was prepared by reductive alkylation of aniline with acetone using copper chromite catalyst at 140° under 50 bar hydrogen pressure<sup>11</sup>. *N*-*n*-Propylaniline was synthesised by direct alkylation of aniline by *n*-propanol over Ce-Y zeolite at 400° in vapour phase. These secondary amines were purified by double-distillation under vacuum. Sodium form of ZSM-5 (I.P.C.L., India) and Y type zeolites (Union Carbide, U.S.A.) were used. H and Ce forms of ZSM-5 and Y zeolites were prepared by ion exchange method. Catalysts were dried at 110° for 2 h followed by calcination at 500° for 4 h. The crystallinity of zeolites was checked by X-ray diffraction using a Philips PW 1730 diffractometer using

nickel filter  $CuK_{\alpha}$  radiation. Surface area of Y and ZSM-5 types were 676–730 and 426–448  $m^{-1} g^{-1}$  respectively. Si/Al ratio was in the range 13.4–43.6. In Ce-Y the degree of exchange of Na to Ce was 67% and in CeZSM-5 the degree of exchange was 58%. These catalysts were used without binders.

Experiments were carried out in a fixed bed down-flow reactor kept in a cylindrical furnace. The catalyst (5 g in powder form) kept in the reactor, was heated to predetermined temperature under slow stream of dry air prior to all reactions. Secondary amine (10% in hexane) was pumped in the reactor by a syringe pump. Liquid products that condensed were collected and analysed by gas chromatography.

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