

STUDIES ON THE ALKYLATION OF ANILINE WITH *n*-PROPANOL AND ISOPROPANOL ON ION-EXCHANGED ZEOLITES

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Alkylation of aniline with *n*-propanol and isopropanol over ZSM-5 and Y-zeolites in vapour phase have been studied under atmospheric pressure to understand the difference in the reaction mechanisms. Alkylation of aniline with *n*-propanol gives *N*-*n*-propylaniline, *o*-*n*-propylaniline and *p*-*n*-propylaniline via the SN_2 mechanistic pathway as well as the products *N*-isopropylaniline, *o*-isopropylaniline and *p*-isopropylaniline via an SN_1 mechanism. Alkylation of aniline with isopropanol produces *N*-isopropylaniline, *o*-isopropylaniline and *p*-isopropylaniline; here both SN_1 and SN_2 mechanisms are operative.

Keywords: alkylation, zeolites, *N*-isopropylaniline

Introduction

Alkylated anilines are industrially important chemicals because of their wide application in the synthesis of dyes [1] and pharmaceuticals [2]. This has spurred much interest in studies aimed at their improved economic production. Zeolites represent an important class of catalysts that offer an attractive alternative to the conventional Friedel-Crafts catalysts used for alkylation which are corrosive and environmentally hostile. Vapour phase methylation of aniline has proved to be particularly facile in the presence of zeolite catalysts [3-6]. Other alkylation routes that have recently been reported include the electrophilic alkylation of aniline by carbonyl compounds using heterogeneous catalysts, like copper chromite in the presence of hydrogen [7-9]. DIXON and BURGoyNE [10] have reported on the alkylation of aniline and substituted anilines over zeolite catalysts. These authors noted that increasing the temperature of the reaction tended to promote C-alkylation. More recently, the alkylation of aniline with ethanol using Na ZSM-5 zeolites containing different SiO_2/Al_2O_3 ratios was reported [11]. We have also observed both N- and C-alkylations in the vapour phase alkylation of aniline with isopropanol over Na, H and Ce forms of ZSM-5 and Y-type zeolites at 200 - 400 °C [12]. A detailed investigation on the above reaction has

now been undertaken using the two isomeric alcohols, *n*-propanol and isopropanol aimed at exploring differences in their reactivity patterns, if any, as well as with a view to determining reaction conditions that influence product selectivities and yields.

Experimental

Aniline, isopropanol and *n*-propanol were commercial samples which were distilled before use. Na-ZSM-5 and Na-Y zeolites were prepared using conventional methods. The H and Ce forms of these were prepared by ion exchange of the sodium forms by treating with ammonium chloride and cerium nitrate solutions, respectively. The degree of cation exchange (Ce for Na) was 87%. After drying at 100 °C for 6 h, the catalysts were calcined for 4 h at 500 °C. Catalysts were used without binder. The crystallinity of zeolites was checked by X-ray diffraction. X-ray diffractograms of zeolite samples were recorded on a Philips PW 1730 X-ray diffractometer using nickel-filtered $CuK\alpha$ radiation; XRD patterns were obtained in a 2θ angle range of 10-50°. The BET surface area of Na-ZSM-5 catalyst was $462\text{ m}^2\text{g}^{-1}$ and Si/Al ratio determined using ICP was 33. BET surface area of Ce-Y catalyst was $747\text{ m}^2\text{g}^{-1}$; Si/Al ratio was 24 (ICP). Experiments were performed in a

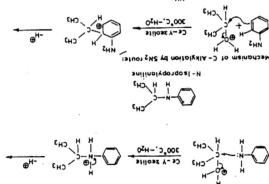
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Table 1 Alkylation of aniline with n-propanol

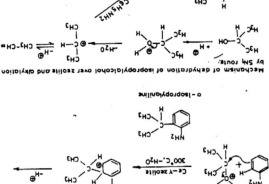
Catalyst	Temp., °C	Flow rate, cm ³ h ⁻¹	Conversion of aniline, mole %	Percentage selectivity of products
Ce-Y	250	10	15.6	5.2
Ce-Y	300	10	24.3	6.6
Ce-Y	350	10	36.6	8.4
Ce-Y	400	10	41.5	9.2
Ce-Y	350	20	32.0	7.4
Ce-Y	350	30	25.0	4.2
Ce-Y	350	40	14.5	3.7
Na-Y	350	10	68.0	6.2
Na-Y	350	10	22.5	7.3
Na-Y	350	10	14.2	10.2
Ce-ZSM5	350	10	32.3	6.8
H-ZSM5	350	10	17.4	8.9
Na-ZSM5	350	10	10.5	9.7
Ce-Y*	450	5	83.2	8.2
		10	67.5	7.8
		10	62.3	7.8
		10	62.3	10.2
		10	67.5	9.4
		10	66.9	8.3
		10	66.2	8.2
		10	67.3	7.8
		10	68.0	8.6
		10	77.2	4.3
		10	72.5	7.6
		10	68.0	9.2
		10	63.3	7.3
		10	64.6	8.8
		10	66.9	7.7
		10	70.0	6.4
		10	64.6	4.4
		10	66.9	5.2
		10	69.9	10.3
		10	66.6	8.5
		10	69.2	7.4
		10	74.4	7.4
		10	68.8	6.8
		10	72.5	7.7
		10	77.3	4.2
		10	86.6	3.7
		10	64.4	6.2
		10	68.0	7.3
		10	67.3	10.2
		10	66.2	6.3
		10	71.1	6.8
		10	82.8	8.9
		10	66.2	9.7
		10	66.9	5.6
		10	67.5	6.0
		10	67.5	7.8
		10	67.5	8.2
		10	67.5	7.6

Wt. of catalyst = 4 g; aniline = n-propanol = 1:2 (mole); Total volume of reactants = 30 cm³; selectivity = (mole % yield of product × 100) / (mole % conversion of aniline); 1 = *N*-*n*-propylaniline; 2 = *o*-*n*-propylaniline; 3 = *p*-*n*-propylaniline; 4 = *N*-isopropylaniline; 5 = *o*-isopropylaniline; 6 = *p*-isopropylaniline; *Wt. of catalyst = 7 g; aniline = n-propanol = 1:3 (mole)

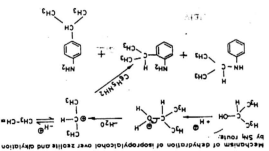
Mechanism of *N*-alkylation by SM3 route:



Mechanism of *C*-alkylation by SM3 route:

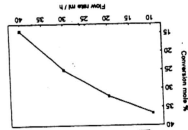


Mechanism of dehydration of isopropylalcohol over zeolite and alkylation



Scheme 1

Fig. 1 Alkylation of aniline with n-propanol over Ce-Y zeolite: temperature = 350°C; wt. of catalyst = 4 g; aniline: n-propanol = 1:2 (mole)



Results and Discussion

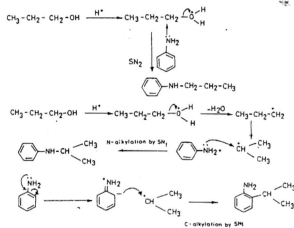
Results of the alkylation of aniline with n-propanol over Na, H and Ce forms of ZSM-5 and Y-type zeolites are given in Table 1. Along with the dominant *N*-*n*-propylaniline, other alkylated products like *ortho*-*n*-propylaniline, *para*-*n*-propylaniline, *N*-isopropylaniline and *ortho*-isopropylaniline were formed. A conceivable route for the formation of *ortho*-isopropylaniline and *para*-isopropylaniline involves the interaction between aniline and propene which is generated *in situ* by the intramolecular dehydration of n-propanol over the zeolite catalyst. Alkylation of aniline with n-propanol over Ce-Y-type zeolite at 450°C under a flow rate of

Table 2 Alkylation of aniline with isopropanol

Catalyst	Flow rate, cm ³ h ⁻¹	Temp., °C	Conversion of aniline, mole %	Percentage selectivity of products			
				1	2	3	4
Ce-Y	10	350	28.3	67.0	24.0	5.3	3.7
H-Y	10	350	12.7	66.3	25.2	5.3	3.2
Na-Y	10	350	8.5	68.2	22.3	6.1	3.4
Ce-ZSM5	10	350	13.8	66.3	27.1	5.4	1.2
H-ZSM5	10	350	7.2	63.2	26.0	6.3	4.5
Na-ZSM5	10	350	5.3	72.0	24.2	2.5	1.3
Ce-Y*	5	450	63.2	60.7	29.4	6.8	3.1

Wt. of catalyst = 4 g; aniline : isopropanol = 1:3 (mole); Total volume of reactants = 30 cm³; selectivity = (mole % yield of product x 100) / (mole % conversion of aniline); 2 = *N*-isopropylaniline; 2 = *o*-isopropylaniline; 3 = *p*-isopropylaniline; 4 = dialkylated products;

*Wt. of catalyst = 7 g; aniline : isopropanol = 1:3 (mole)

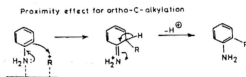


Scheme 2

alkylated product at higher contact time is that it suffers isomerization and dealkylation over zeolite. The conversion of aniline increased with the increase in acidity of the catalyst. Thus the conversion of aniline was only 14.2% over NaY zeolite. C-alkylated products are *o*-*n*-propylaniline, *p*-*n*-propylaniline, *o*-isopropylaniline and *p*-isopropylaniline. If there was only direct alkylation by intermolecular condensation between aniline and *n*-propanol, the product would be *N*-*n*-propylaniline, *o*- and *p*-*n*-propylanilines. So it is concluded that *N*-*n*-alkylation takes place by a SN₂ type reaction (Scheme 2), while the formation of *ortho* and *para*-isopropylanilines is by a carbenium ion mechanism involving propene (Scheme 1). Such observations have been reported in electrophilic substitution of phenol by *n*-propanol and isobutanol over alumina [13]. Propene was formed in the process by dehydration of the alcohol over zeolite as well as by dealkylation of *N*-alkylated product over catalyst.

Alkylation of Aniline by Isopropanol

Results of the alkylation of aniline with isopropanol over Ce, H and Na forms of zeolite catalysts are given in Table 2. The major product of the reaction is *N*-isopropylaniline. The yield of the *ortho*-isomer is consistently more than that of the *para*-isomer. This is explicable in terms of a proximity effect, illustrated in Scheme 3. The yield of *N*-isopropylaniline in this reaction was relatively less than the corresponding yield



Scheme 3

of *N*-*n*-propylaniline in the alkylation of aniline with *n*-propanol. The reason for this observation is that *N*-*n*-propylaniline is more stable than *N*-isopropylaniline. This is supported by our previous study [14] on the reaction of *N*-isopropylaniline over zeolite at 300 °C, where it was observed that *N*-isopropylaniline isomerised to give *o*-isopropylaniline and *p*-isopropylaniline as well as dealkylated to give aniline and propene [14]. Among the C-alkylated products, the *ortho*-isomer has been reported as the major product in the study of alkylation of aniline with alkenes over a variety of acid catalysts such as Y-zeolite, BF₃, HCl and silica-alumina [15]. BURGoyNE and DIXON [15] and HART and KOSAK [16] reported a mechanism involving a cyclic transition state to account for the *ortho*-selectivity, irrespective of whether the catalyst is homogeneous or heterogeneous. It is reasonable to believe that *ortho*-selectivity is a consequence of the proximity of the carbenium ion present on the catalyst surface to the *ortho* position of aniline. Alkylating agent is adsorbed on the surface of the catalyst through the heteroatom. *N*-*n*-propylaniline over zeolite at 300 °C in vapour phase is isomerised to form *o*-isopropylaniline and *p*-isopropylaniline and dealkylated to give aniline and propene under identical reaction conditions. Conversion of *N*-isopropylaniline was (dealkylation and isomerisation) more than that of *N*-*n*-propylaniline over zeolites. The effect of flow rate on alkylation of aniline by isopropanol was studied (Fig. 2). It was observed that the conversion of aniline was only 4.7% under a flow rate of 30 cm³ h⁻¹ (Fig. 3). But the selectivity of *N*-isopropylaniline was 92.3 under a flow rate of 30 cm³ h⁻¹. The conversion of aniline increased to 26.0% under a flow rate of 5 cm³ h⁻¹; but the *N*-alkylation selectivity decreased to 54.8% (Table 3). These results indicate that with longer times, the *N*-alkylated product suffers dealkylation to aniline and propene as well as gets isomerised to give C-alkylated products. The conversion of aniline was increased to 63.2% at 450 °C under a flow rate of 5 cm³ h⁻¹ using 7 g catalyst. From a separate

Table 3 The effect of flow rate in the reaction between aniline and isopropanol over Ce-Y zeolite

Flow rate, $\text{cm}^3 \text{h}^{-1}$	Temp., $^{\circ}\text{C}$	Conversion of aniline, Mole %	Mole % selectivity of products
5	350	26.0	54.8
10	350	23.3	63.2
15	350	20.4	68.0
20	350	6.8	76.0
25	350	5.6	87.0
30	350	4.7	92.3
			5.6
			20.1
			22.8
			9.3
			7.2
			2.0
			3.0
			14.0
			28.2
			2.1

Wt of catalyst = 3 g; aniline: isopropanol = 1:3 (mole); Total volume of reactants = 30 cm^3 ; selectivity = (mole % yield of product $\times 100$) / (mole % conversion of aniline); 1 = *N*-isopropylaniline; 2 = *o*-isopropylaniline; 3 = *p*-isopropylaniline; 4 = dialkylated product

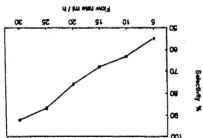


Fig. 3 Alkylation of aniline with isopropanol. Effect of flow rate on selectivity of *N*-isopropylaniline: temperature = 350 $^{\circ}\text{C}$; wt. of catalyst = 3 g; aniline: isopropanol = 1:3 (mole)

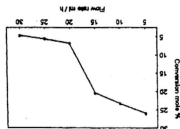


Fig. 2 Alkylation of aniline with isopropanol over Ce-Y zeolite: temperature = 350 $^{\circ}\text{C}$; wt. of catalyst = 3 g; aniline: isopropanol = 1:3 (mole)

study of time on stream it was observed that the catalyst gets deactivated after 13 cycles (each cycle of experiment of one hour duration) of operation. The present investigation does not reveal remarkable difference in shape selectivity over Na or Ce form of zeolite.

Conclusions

Alkylation of aniline by *n*-propanol over zeolites produced *N*-*n*-propylaniline (major product), *ortho* and *para*-*n*-propylanilines through the SN_2 mechanism, and *N*-isopropylaniline, *o*- and *p*-isopropylanilines through the SN_1 mechanism. Alkylation of aniline by isopropanol over zeolites produced *N*-isopropylaniline as the major product. The selectivity of *N*-isopropylaniline is higher than *ortho* and *para*-isopropylanilines at 250 $^{\circ}\text{C}$ under high flow rate. This clearly indicates that C-alkylation is the result of isomerisation of *N*-isopropylaniline which occurs at higher temperatures and longer contact times.

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