AMINATION OF BUTANOL ON Na FORMS OF ZEOLITES

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Amination of aliphatic alcohols by ammonia is usually conducted in the presence of dehydrating catalysts such as Al_2O_3 , ThO_2 , and gumbrin with H_2SO_4 [1]. Amination on these catalysts is associated with the formation of ethers, aldehydes, nitriles, and olefins, which significantly reduces the selectivity of the process [1]. According to [2, 3], amination of methanol and phenol by ammonia takes place on zeolites. Amination of aliphatic alcohols containing more than one carbon atom on zeolites is only described in [4].

The study of Na forms of zeolites containing no acid sites responsible for many side reactions for amination is of special interest. Amination of l-butanol by ammonia on Na forms of zeolites with a different SiO_2/Al_2O_3 ratio and a different backbone structure was studied in the present article.

EXPERIMENTAL

The catalytic experiments were conducted in a flow-type setup at 0.1 MPa in the 250-450°C range. Zeolites with the following SiO_2/Al_2O_3 ratio were used: NaA, 2.0; NaX, 2.9; NaY, 4.2, 4.4, 5.2, 5.8; Na-mordenite (NaM), 11.9. High-silicon zeolite (Na HSZ, $SiO_2/Al_2O_3 = 60$) was prepared with tetrabutylammonium bromide. Al_2O_3 was prepared by the method in [5]. The feed rate was $8.57 \cdot 10^{-2}$ mole/h for NH₃ and $1.46 \cdot 10^{-2}$ mole/h per 1 g of catalyst for 1-butanol. In the experiments with NaX, where the optimum conditions of amination were determined, the feed rate was varied in the range of $0.94 \cdot 10^{-2} - 8.57 \cdot 10^{-2}$ mole/h for NH₃ and $0.50 \cdot 10^{-2} - 5.83 \cdot 10^{-2}$ mole/h per 1 g of catalyst for 1-butanol. The catalyst underwent preliminary treatment at 500°C for 4 h in an air current, for 2 h in an He current, and with ammonia at the experimental temperature until NH₃ appeared at the reactor outlet. A mixture of NH₃ and 1-butanol was then delivered to the reaction zone. The reaction products were analyzed by column GLC (3 m long, 3 mm in diameter) packed with Chromosorb WAW containing 4% KOH and 16% PEG-425 with Apiezon L (2:1)

DISCUSSION OF RESULTS

The effect of the feed rate of 1-butanol (Fig. 1) and the ammonia:alcohol molar ratio (Fig. 2) on the activity and selectivity of the catalyst and on the composition of the amines formed in the reaction of amination of 1-butanol by ammonia was studied on NaX zeolite. The activity of the catalyst was evaluated with respect to the yield of amines for the alcohol delivered and the selectivity was evaluated with respect to the yield of amines for the alcohol delivered was observed with a molar ratio of 1-butanol of $0.86 \cdot 10^{-2} - 1.75 \cdot 10^{-2}$ mole/h per 1 g of catalyst (cf. Fig. 1a). The yield of amines for the converted alcohol remained constant when the feed rate of the alcohol was varied in the range of $0.86 \cdot 10^{-2} - 5.83 \cdot 10^{-2}$ mole/h per 1 g of catalyst (see Fig. 1a). The composition of the amines formed did not change with a feed rate of 1-butanol of $0.7 \cdot 10^{-2} - 2.9 \cdot 10^{-2}$ mole/h per 1 g of catalyst (see Fig. 1b).

When the ammonia: alcohol molar ratio increased from 0.5 to 2.0, the yield of amines on Na zeolite increased from 23 to $\sim 60\%$ for the alcohol delivered and from 40 to $\sim 80\%$ for the alcohol converted (see Fig. 2a). A further increase in this ratio to 5 did not affect the yield of amines (see Fig. 2a). The composition of the amines formed was not dependent on the ammonia: alcohol molar ratio (see Fig. 2b).

The yield of amines on all catalysts initially increased as the reaction temperature: increased from 250 to 400°C and then decreased due to the occurrence of side reaction

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Fig. 1. Dependence of the yield (a) and composition of the animes (formed b) on the feed rate of the alcohol (v) on NaX zeolites: 1) yield of amines for the alcohol delivered; 2) yield of amines for the alcohol converted; 3) butylamine; 4) dibutylamine; 5) tributylamine. NH_3 feed rate of $8.57 \cdot 10^{-2}$ mole/h, reaction temperature of 400°C.

Fig. 2. Dependence of the yield (a) and composition (b) of the amines formed on the NH_3 :alcohol molar ratio on NaX zeolite. 1-Butanol feed rate of $1.46 \cdot 10^{-2}$ mole/h per 1 g of catalyst, reaction temperature of 400°C. See Fig. 1 for explanation of 1-5.

TABLE 1. Amination of 1-Butanol by Ammonia on Na Forms of Zeolites at 400°C (NH₃ feed rate of $8.57 \cdot 10^{-2}$ mole/h, 1-butanol feed rate of $1.46 \cdot 10^{-2}$ mole/h per 1 g of catalyst)

Catalvst	Yield of	amines, %	Catalvst	Yield	l of amines, %
	for alcohol delivered	for alcohol converted		for alcohol delivered	for alcohol converted
NaA NaX NaY *	6,4 58,7 51,9	63,5 78,7 80,2	NaM NaM† NaHSZ	0 2,3 22,0	0 23,7 73,6

 $*SiO_2/Al_2O_3 = 4.2$. [†]1-Butanol feed rate of $0.3 \cdot 10^{-2}$ mole/h per 1 g of catalyst.

(Fig. 3a). Zeolites Y and X were the most active and selective in amination (Figs. 1 and 2, Table 1). The narrow-pore Na forms of zeolites A and mordenite exhibited the lowest activity of the catalysts studied (see Table 1). The size of the eight-membered windows joining the internal cavities in zeolite A did not exceed 4 Å, while in the Na form of mordenite, the cations located in the large channels decreased the effective diameter of these channels to 3.9 Å [6]. The small diameter of the channels in these zeolites apparently prevents penetration of the 1-butanol molecules into the internal cavities of NaA and NaM zeolites. NaHSZ was more active than Na-mordenite (see Table 1), although the diameter of its channels is smaller than in the mordenite. According to the adsorption measurements, the Na⁺ cations in zeolites synthesized with organic substances do not affect the accessibility of the channels for large organic molecules, while the presence of Na⁺ cations in the mordenite sharply decreases the adsorption of such molecules as benzene or cyclohexane [7]. In addition, it is also possible that weak acid sites formed in the decomposition of the organic substances in NaHSZ zeolite could play some role in amination [8].

The catalytic properties of the zeolites were compared with Al_2O_3 (see Fig. 3, Table 2), which is a well-known catalyst of amination [1], in amination of 1-butanol by ammonia. The



Fig. 3. Effect of the reaction temperature on the yield of amines for the alcohol delivered (a) and converted (b) on the catalysts: NaX (1), NaY-4,4 (2), NaHSZ (3), and Al_2O_3 (4).

Fig. 4. Dependence of the yield of amines at 350° C on the number of nonlocalized Na⁺(n) cations in the unit cell of faujasites.

activity of Al_2O_3 is similar to the activity of Na-faujasites (see Fig. 3a), but amination on Al_2O_3 is accompanied by significant side reactions which strongly decrease the selectivity of the process (see Fig. 3b). The reduced selectivity of Al_2O_3 is apparently due to the fact that there is a significant number of acid sites which are active in the transformation of alcohols into olefins on the surface of Al_2O_3 [9].

Butylamine (BA), dibutylamine (DA), and tributylamine (TA) are formed in the reaction on zeolites (Table 2). The formation of BA takes place as the result of the reaction of 1-butanol with ammonia:

$$BuOH + NH_3 \rightarrow BuNH_2 + H_2O \tag{1}$$

DA and TA are obtained by substituion of the hydrogen in the amino group of BA;

 $BuOH + BuNH_2 \rightarrow Bu_2NH + H_2O$ (2)

$$BuOH + Bu_2NH \rightarrow Bu_3N + H_2O$$
(3)

As the data in Table 2 show, an increase in the reaction temperature from 250 to 350° C results in an increase in the concentration of DA and TA in the amines formed (see Table 2). The yield of BA increases according to reaction (1) with an increase in the temperature. This causes reaction (2), i.e., the formation of DA, and the increase in the yield of DA in turn favorably affects reaction (3). BA and DA are stronger bases than NH₃, and they are apparently adsorbed better on the surface of the catalyst, which facilitates the occurrence of reactions (2) and (3) and results in an increase in the concentration of DA and TA. With a further increase in the temperature to 450° C, the concentration of BA increases in the amines formed (see Table 2). In this case, the degree of conversion of the alcohol is relatively high (it attains 100% in many cases), which impedes the occurrence of reactions (2) and (3) and subsequently the formation of DA and TA. In addition, the reaction of NH₃ with DA and TA cannot be excluded:

> $Bu_2NH + NH_3 \rightarrow 2BuNH_2$ $Bu_3N + NH_3 \rightarrow Bu_2NH + BuNH_2$

which also results in an increase in the concentration of BA in the amines formed.

TABLE 2. Composition of Amines Formed in Amination of 1-Butanol by Ammonia (NH₃ feed rate of $8.57 \cdot 10^{-2}$ mole/h, 1-butanol feed rate of $1.46 \cdot 10^{-2}$ mole/h per l g of catalyst)

						Reaction	temperatu	re, °C							
Catalyst		250			300			350			400			450	
	BA	DA	Δ	BA	DĄ	TA	BA	DA	TA	BA	DA	TA	BA	DA	TA
NaA NaX NaY * NaM † Na HSZ	88,9	11,1	10111	38.8 72,1	44,9 27,9	16,3 1 - 1	27,5 27,5 63,2 70,2	55.8 33,58 29,2	16,7 3,3 0	63,8 57,2 66,2 14,8 59,1	36,2 37,8 30,3 67,3 39,8	$\begin{array}{c} 0 \\ 4,9 \\ 3,5 \\ 1,1 \\ 1,1 \end{array}$	98,9 72,4 62,8	$^{+1.4}_{-26,7}$	0,0
Al ₂ O ₃	95,2	4,8	0	1 79,3 1	20,7	0	52,7	45,4	1,9	92,2	7,8	0	100,0	0	0

^{*}SiO₂/Al₂O₃ = 4.4. [†]1-Butanol feed rate of 0.3·10⁻² mole/h per 1 g of catalyst.

Let us examine the possible causes of the activity of the zeolites in the reaction studied. As noted previously, wide-pore NaY and NaX zeolites have the highest activity in the amination of 1-butanol (see Fig. 3, Table 1). In most reactions of the transformation of hydrocarbons on decationized faujasites or on faujasites containing multiply charged cations, Y zeolites are more active than X zeolites. In these zeolites, the topology of the backbone and consequently the pore structure are the same [10]. The increased activity of Y zeolites in reactions of the carbonium ion type is usually correlated with their stronger acid sites [10]. The higher activity of X zeolites in the amination of butanol suggests that Na⁺ cations, whose number is greater in the unit cell of X zeolite than in the unit cell of Y zeolite, are the carriers of the catalytic activity in this reaction. Since the number of localized cations is almost the same in faujasites [6], it is not very probable that the observed differences in the activity of X and Y zeolites are due to localized cations. On the contrary, the number of nonlocalized cations in the unit cell of zeolite is essentially dependent on the modulus of the zeolite and is much greater in X zeolite than in Y zeolite. According to [11], only nonlocalized Na⁺ cations are capable of dissociatively adsorbing H_2S . It is possible to hypothesize that nonlocalized Na⁺ cations are the active sites in the amination of 1-butanol by ammonia. This is confirmed by the linear dependence of the activity of faujasites with a different SiO_2/Al_2O_3 ratio on the number of nonlocalized Na⁺ cations (Fig. 4), calculated with the equation

$$n = \frac{192}{1+R} - 48$$

where n is the number of nonlocalized cations; R=Si/Al, and 48 is the number of localized cations [6].

According to [12], the heat of adsorption of $\rm NH_3$ by the cations is greater the more weakly they are bound with the backbone. The number of nonlocalized cations increases with a decrease in the modulus of the zeolite, the bond of the actions with the backbone becomes weaker, and the strength of the bond of the adsorbed $\rm NH_3$ with the Na⁺ cation correspondingly increases, which probably intensifies the activation of $\rm NH_3$ and facilitates its reaction with the alcohol molecules.

CONCLUSIONS

1. The capacity of zeolites in the Na form to conduct the reaction of amination of 1butanol by ammonia was demonstrated. The activity and selectivity of the zeolites increase in the order Na-mordenite < NaA < NaHSZ < NaY < NaX.

2. Nonlocalized sodium cations are the carriers of the catalytic activity in the reaction of amination on Na forms of zeolites.

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