Base catalysis on zeolites in the formaldehyde–dimethylamine transformations

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Abstract

The character of catalytic transformations in the 'dimethylamine–formaldehyde–water' system was studied using ZSM-5 and Beta zeolites as catalysts, in which the concentration of strong protic centers has been varied by the chemical modification. It is shown that both the acidity of the zeolite and reaction temperature determine the direction of the transformation in the system. The decrease of these both parameters results in the growth of N,N-dimethylformamide yield, while the increase of the acidity of the zeolite and reaction temperature leads to considerable predominance of 1,3,5-triazine derivative in the products. The possibility of the creation of basic catalytic sites by the weak interaction of dimethylamine molecules with low-acidic zeolite during the reaction is supposed to be a key factor, which determines the prevalent transformation route in the system.

Keywords: Beta zeolite; Chemical modification; N,N-Dimethylformamide; Formaldehyde; Methylamines; 1,3,5-Trimethylhexahydro-1,3,5-triazine; ZSM-5 zeolite

1. Introduction

The use of zeolites of different compositions and structure types as catalysts for the reactions of selective organic and petrochemical syntheses has gained significant interest over the past several years [1–3]. The primary driving forces for this are no longer only markets and process economics, but also the development of new products and processes, and environmental considerations. Most of the reactions studied are typically acid-catalyzed ones and therefore require zeolites to be applied in decationated H forms. At the same time, a lot of reactions of selective organic synthesis are known as base-catalyzed ones, and application of zeolites as catalysts for these reactions remains a practically unelaborated problem so far.

In this work the approach to realize the base-catalyzed transformations on zeolites is considered in terms of the example of the simplest and simultaneously typical base-catalyzed reaction.

2. Experimental

Catalysts were prepared by the treatment of H forms of ZSM-5 and Beta type zeolites with aqueous solutions of corresponding modifiers followed by drying and calcination [4,5]. Magnesium nitrate and boric acid were used as modifiers. Parent zeolites had the following characteristics: for ZSM-5 – molar ratio $SiO_2/Al_2O_3 = 95$, typical size of crystals $= 0.5$–1.5 μ, the surface area of mesopores $= 61$ m^2/g; for BETA – molar ratio

Table 1
Types of acid centers and their concentrations (μmol/g) in the investigated zeolites according to IR data

Sample	Modifier	Strong protic centers $\nu_{OH} = 3610$ cm^{-1}	Strong aprotic centers $\nu_{CO} = 2220$–2230 cm^{-1}	Medium-strength aprotic centers $\nu_{CO} = 2210$–2215 cm^{-1}
ZSM-5-1	–	120	18	no data
ZSM-5-2	magnesium	80	absent	29
ZSM-5-3	boron	13	absent	10
ZSM-5-4	boron	4	absent	absent
Beta-1	–	94	24	25
Beta-2	magnesium	18	24	no data
Beta-3	magnesium	6	20	no data
Beta-4	boron	absent	absent	25

$SiO_2/Al_2O_3 = 42$, typical size of crystals = 500–1000 Å, the surface area of mesopores = 137 m^2/g. The size of zeolite crystals was estimated in TEM micrographs obtained on a JEM-100C transmission microscope. The surface area of mesopores (specific external surface area of zeolite crystals) was calculated from isotherms of low-temperature nitrogen adsorption by comparative method [6].

2.1. IR spectroscopy investigations

Sample pellets (8–10 mg/cm^2) were calcined in IR cell at 450°C in air for 1 h and then in vacuum (10^{-5} Pa) for 1 h. Spectra were recorded using UR-20 spectrometer, specially modified for operating in wide temperature range.

Concentration of Brønsted (protic) centers was calculated from both the intensity of the OH group band [7] ($\nu_{OH} = 3610$ cm^{-1}, $A_0 = 7$ cm^{-1}/μmol) and the intensity of corresponding band of OH groups in complexes with CO [8] ($\nu_{OH...CO} = 3310$ cm^{-1}, $A_0 = 57$ cm^{-1}/μmol) according to the equation:

$$C(\mu\text{mol/g}) = (A_0\rho)^{-1}\int\log(T_0/T)\,d\nu,$$

where A_0 is a coefficient of integral absorption, cm^{-1}/μmol; ρ is surface density of a pellet, g/cm^2; T_0 and T are transmissions of an IR beam for an individual line through the pellet before and after CO adsorption, respectively, %.

2.2. Catalytic studies

Investigation of the selectivity of the catalysts was carried out under steady state conditions toward conversion of the dimethylamine (DMA)–formaldehyde (F)–water mixture in a flow quartz reactor at atmospheric pressure for the following ranges of reaction parameters: temperature inside catalyst bed – 140–320°C; weight hourly space velocity (WHSV) to starting mixture – 1.3 ± 0.2 and 2.8 ± 0.2 h^{-1}. Starting reaction mixtures were prepared from titrated aqueous solutions of DMA and F, molar ratio (DMA/F) in them was varied in the range of 0.7–1.9, while molar ratio (H_2O/F) was approximately constant and in the range 9.8–12.5.

GC system was used for analysis of the reaction products. Identification of products was carried out by ^{1}H and ^{13}C NMR using a CXP-300 and a MSL-400 Bruker spectrometers.

3. Results

Main characteristics of acidic properties of the zeolites studied are presented in Table 1. The data for most of the samples are identical with the data in Refs. [4,5].

Under all reaction conditions mentioned above only three products were found in gas phase at transformations of the DMA–F–H_2O mixtures on all catalysts. The reaction products identified with NMR were the following: trimethylamine, N,N-
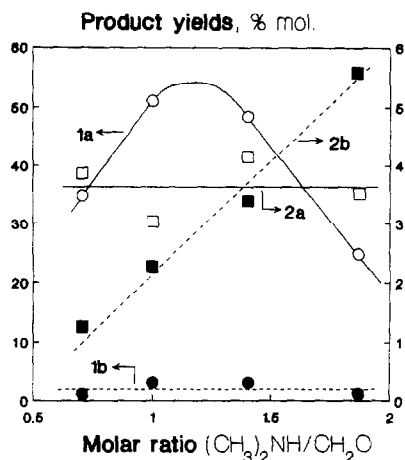
Fig. 1. Dependence of the yields of DMF (curves a, open circles and squares) and TAZ (curves b, black circles and squares) for Beta-4 at $190 \pm 5°C$ (curves 1) and for ZSM-5-1 at $220 \pm 2°C$ (curves 2) on DMA/F molar ratio in starting reaction mixture. *Other reaction conditions*: H_2O/F molar ratio in starting mixture $= 10.8 \pm 1.0$; WHSV to starting mixture $= 1.3 \pm 0.2 \ h^{-1}$.
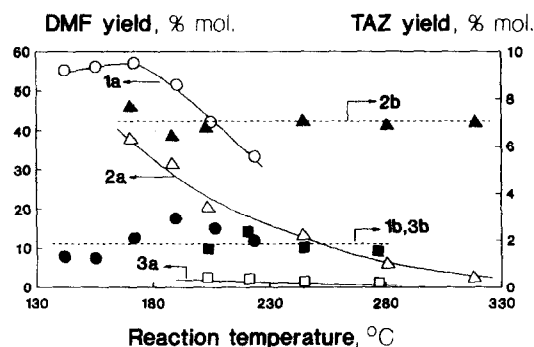

Fig. 2. Dependence of the yields of DMF (curves a, open circles, triangles and squares) and TAZ (curves b, black circles, triangles and squares) on the reaction temperature during conversion of the mixture with starting molar ratio DMA/F = 1.0 on Beta-4 (curves 1), ZSM-5-4 (curves 2) and ZSM-5-1 (curves 3). *Other reaction conditions*: H_2O/F molar ratio in starting mixture $= 9.8$; WHSV to starting mixture $= 1.3 \pm 0.2 \ h^{-1}$.

dimethylformamide (DMF) and 1,3,5-trimethyl-hexahydro-1,3,5-triazine (TAZ). Here, however, the ratio of DMF and TAZ yields calculated with respect to formaldehyde passed through the catalyst bed depends strongly on both reaction conditions and acidic properties of zeolites.

The influence of DMA/F molar ratio in starting mixture on DMF and TAZ yields was studied for two zeolite samples with sharply different concentrations of strong protic centers (Fig. 1). As seen in the figure, the dependence of the DMF yield for the zeolite with the lowest acidity (Beta-

4, Table 1) has a maximum near the ratio DMA/F = 1 (curve 1a), while the yield of TAZ is approximately constant and relatively low (level 1b). The DMF yield for this sample exceeds the TAZ yield more than one order of magnitude. By contrast, for the zeolite with the highest acidity (ZSM-5-1, Table 1) the DMF yield is approximately constant (level 2a), while the TAZ yield increases monotonically attaining the maximum value near the ratio DMA/F = 2 (curve 2b). But, the yields of both products on ZSM-5-1 sample are very low and close one to another.

The influence of reaction temperature on DMF and TAZ yields was studied for two compositions of starting mixtures with molar ratios DMA/F = 1 (Fig. 2) and DMA/F = 1.9 (Fig. 3) and also for two zeolites with sharply different concentrations of strong protic centers. As seen in Fig. 2 for the conversion of the reaction mixture in optimum composition for DMF formation (Fig. 1), the yield of this product for every zeolite studied increases under decreasing reaction temperature (curves 1a–3a). Here, the value of DMF yield at constant temperature turns out to be the higher the lower is the concentration of strong protic centers in a zeolite. At the same time, the TAZ yield under conversion of the same mixture with DMA/F = 1 (Fig. 2) is very low and is practically independent of reaction temperature (levels 1b–3b). When the composition of reaction mixture is optimum for TAZ formation (Fig. 1), i.e. with the ratio DMA/
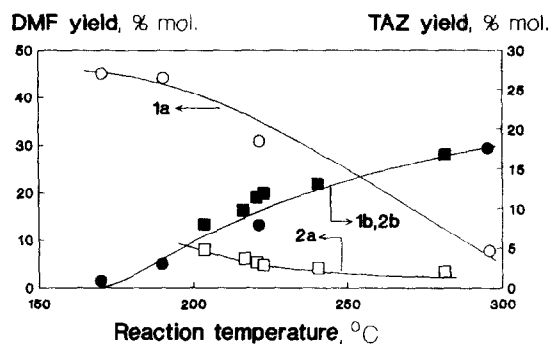

Fig. 3. Dependence of the yields of DMF (curves a, open circles and squares) and TAZ (curves b, black circles and squares) on the reaction temperature during conversion of the mixture with starting molar ratio DMA/F = 1.9 on Beta-4 (curves 1) and ZSM-5-1 (curves 2). *Other reaction conditions*: H_2O/F molar ratio in starting mixture $= 12.5$; WHSV to starting mixture $= 2.8 \pm 0.2 \ h^{-1}$.
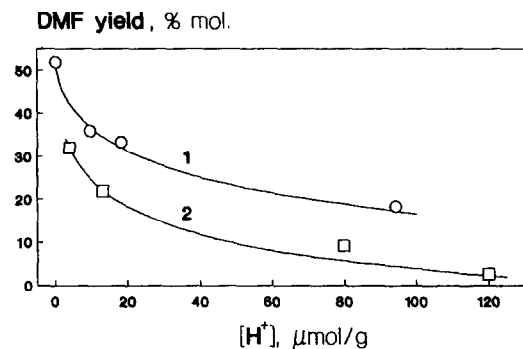
DMF yield, % mol.

Fig. 4. Dependence of the DMF yields on the concentration of strong protic centers in Beta (1) and ZSM-5 (2) zeolites. *Reaction conditions*: reaction temperature $= 200 \pm 5°C$; DMA/F molar ratio in starting mixture $= 1.0$; H_2O/F molar ratio in starting mixture $= 9.8$; WHSV to starting mixture $= 1.3 \pm 0.2\ h^{-1}$.

$F = 1.9$, the DMF yield increases too under decreasing reaction temperature (Fig. 3, curves 1a, 2a) and, like for starting mixture with the ratio DMA/F $= 1$, the value of the DMF yield at constant temperature also becomes higher the lower the concentration of strong protic centers in a zeolite. However, unlike the transformation of the starting mixture with the ratio DMA/F $= 1$ (Fig. 2), for this mixture composition the TAZ yield increases sharply with increasing reaction temperature (Fig. 3, curves 1b, 2b) independently of zeolite acidity. As a result, TAZ becomes almost the only reaction product at relatively high temperatures under transformation of starting mixture with the ratio DMA/F $= 1.9$.

The dependence, mentioned above, of the DMF yield on the acidic properties of the zeolites under study for specified reaction conditions are summarized in Fig. 4. As seen in the figure, the DMF yield increases for both Beta and ZSM-5 zeolites with decreasing concentration of strong protic centers in the catalysts.

4. Discussion

The results of the study of catalytic properties of both parent and chemically modified zeolites toward joint transformation of dimethylamine and formaldehyde in presence of water show that a decrease of both catalyst acidity (Fig. 4) and reac-

tion temperature (Figs. 2, 3) leads to increasing the DMF yield. At the same time, the TAZ yield increases with increasing reaction temperature under transformation of the mixture with starting molar ratio DMA/F $= 1.9$ only (Figs. 2, 3).

The character of the dependence of the yields of DMF and TAZ on the composition of starting reaction mixture (Fig. 1), where the maximum DMF yield is observed near the ratio DMA/F $= 1$, while the greatest TAZ yield – at the ratio DMA/F $= 1.9$, admits the supposition, that the indicated compositions of the starting mixtures are close to the stoichiometry of the routes of DMF and TAZ formation, and allows us to describe the observed transformations by schemes (A) and (B) (Fig. 5).

Disproportionation of aldehyde by Cannizzaro's reaction to produce alcohol and carboxylic acid is the basis of the scheme (A). Further interaction of these semiproducts with DMA results in formation of trimethylamine and DMF as the final products. The total stoichiometry of interaction of DMA with F by this route corresponds to the ratio DMA/F $= 1$.

$$2CH_2O + H_2O \xrightarrow{A1} CH_3OH + HCOOH$$

A2' $\Bigg/ \left(+ (CH_3)_2NH \atop - H_2O \right) \Bigg\backslash$ A2''

$(CH_3)_3N \qquad\qquad HCON(CH_3)_2$

$$2(CH_3)_2NH \xrightarrow{B1} CH_3NH_2 + (CH_3)_3N$$

$(+ CH_2O) \ \Bigg\downarrow^{B2'} \ (- H_2O)$

$[CH_3N-CH_2]$

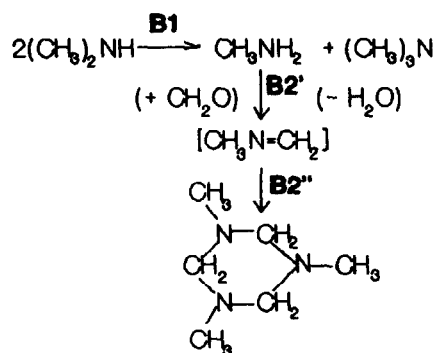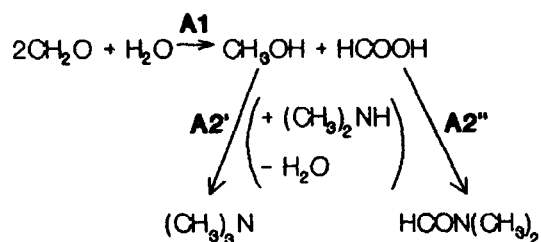$CH_3 \ \Bigg\downarrow^{B2''}$

Fig. 5. Main reaction routes of the formaldehyde–dimethylamine transformations on the zeolites.

By contrast, the first stage of the scheme (B) is a disproportionation of dimethylamine to mono- and trimethylamines, from which monomethylamine only is capable to react with aldehyde to produce TAZ. The total stoichiometry of interaction of DMA with F via this route corresponds to the ratio DMA/F = 2. However, since the yield of TAZ is found to be significant at relatively high reaction temperatures and is independent of both acid and structural characteristics of the zeolites (see the coincidence of the curves 1b and 3b in Fig. 2 and the curves 1b and 2b in Fig. 3), all the reactions of the route (B) seem not to be influenced by the catalysts studied.
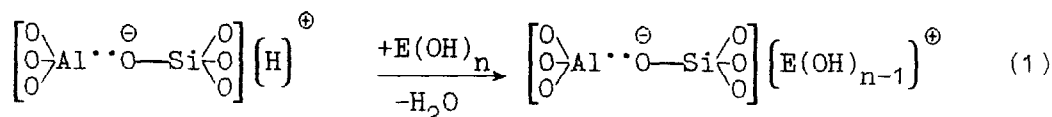
Unlike the scheme (B), the first stage of the scheme (A) is a base-catalyzed reaction and is known [9] to require the participation of a weak basic center. Since this type of center is absent in the zeolite catalysts in their starting forms (before reaction), it must be supposed that these centers may appear in the catalyst during the reaction under direct participation of reaction mixture components. Moreover, since the DMF yield grows with decreasing reaction temperature (Figs. 2, 3), then at fixed, other experimental conditions this growth of the yield may be due to the increase of the concentration of such basic sites with decreasing reaction temperature. In addition, as the DMF yield grows rapidly with decreasing the concentration of strong protic centers in catalysts (Fig. 4), so the lowering of the concentration

of strong protic centers gives more possibilities for the appearance of weak basic sites.
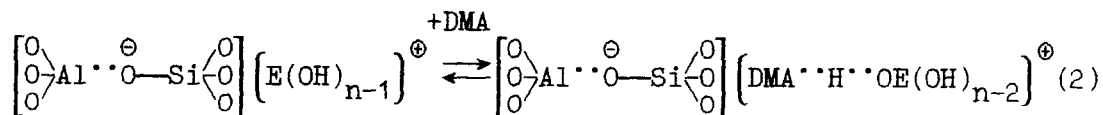
Indeed, in accord with ideas developed earlier [4,5], the chemical modification of highly acidic H forms of zeolites results not only in a decrease of the concentration of strong protic centers in samples (table), but also leads simultaneously to the formation of secondary protic centers according to Scheme 1.

The strength of the latter is supposed [5] to be influenced by the nature of the central atom (E) and was significantly lower in all systems studied as compared with the strength of the 'bridged' OH group in the H form of a zeolite. In this case, DMA molecules, adsorbed on the weak protic center, may behave as a catalytic basic site in the disproportionation of F via the scheme (A). The low acidity of the secondary center ensures its weak interaction with DMA molecule via Scheme 2 unlike ordinary protonation on the strong center via Scheme 3. Being reversibly adsorbed on weak protic sites, DMA molecules keep their basic properties unchanged, and the concentration of weakly bound DMA molecules should increase upon decreasing both the reaction temperature and the concentration of strong protic centers.
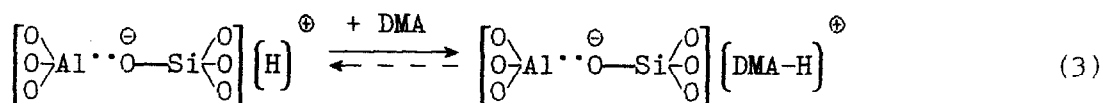
It is noteworthy (Fig. 4) that the DMF yield on Beta zeolites is markedly higher compared with that on ZSM-5 zeolites under the same reaction conditions and at similar concentrations of protic centers. It seems inconceivable that the higher

$$\left[\begin{matrix} O \\ O \\ O \end{matrix} \!\!\!\!>\!\! Al \cdots O\!\!-\!\!Si \!\!<\!\! \begin{matrix} O \\ O \\ O \end{matrix} \right]^{\ominus} \!\! \left[H \right]^{\oplus} \quad \xrightarrow[-H_2O]{+E(OH)_n} \quad \left[\begin{matrix} O \\ O \\ O \end{matrix} \!\!\!\!>\!\! Al \cdots O\!\!-\!\!Si \!\!<\!\! \begin{matrix} O \\ O \\ O \end{matrix} \right]^{\ominus} \!\! \left[E(OH)_{n-1} \right]^{\oplus} \qquad (1)$$

Scheme 1.

$$\left[\begin{matrix} O \\ O \\ O \end{matrix} \!\!\!\!>\!\! Al \cdots O\!\!-\!\!Si \!\!<\!\! \begin{matrix} O \\ O \\ O \end{matrix} \right]^{\ominus} \!\! \left[E(OH)_{n-1} \right]^{\oplus} \quad \xrightarrow{+DMA} \quad \left[\begin{matrix} O \\ O \\ O \end{matrix} \!\!\!\!>\!\! Al \cdots O\!\!-\!\!Si \!\!<\!\! \begin{matrix} O \\ O \\ O \end{matrix} \right]^{\ominus} \!\! \left[DMA \cdots H \cdots OE(OH)_{n-2} \right]^{\oplus} \quad (2)$$

Scheme 2.

$$\left[\begin{matrix} O \\ O \\ O \end{matrix} \!\!\!\!>\!\! Al \cdots O\!\!-\!\!Si \!\!<\!\! \begin{matrix} O \\ O \\ O \end{matrix} \right]^{\ominus} \!\! \left[H \right]^{\oplus} \quad \xleftarrow{+\ DMA} \quad \left[\begin{matrix} O \\ O \\ O \end{matrix} \!\!\!\!>\!\! Al \cdots O\!\!-\!\!Si \!\!<\!\! \begin{matrix} O \\ O \\ O \end{matrix} \right]^{\ominus} \!\! \left[DMA\!-\!H \right]^{\oplus} \qquad (3)$$
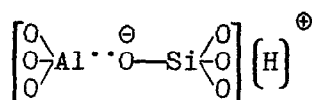
Scheme 3.

DMF yield on Beta zeolites is due to some molecular sieve effect, in particular, due to significantly larger pore size in the case of this zeolite. The assumption that the transformations observed occur predominantly on the external surface of zeolite crystals seems to be more appropriate. Indeed, under high concentration of water in the reaction mixture and relatively low temperature internal volume of the crystals may be inaccessible for reagents at all, e.g. because of water adsorption. Whilst characteristic size of the crystals of investigated Beta zeolite is significantly smaller, and their external surface is markedly larger as compared to the same values for investigated ZSM-5 zeolite.

As a whole, the direction of primary transformation in the 'dimethylamine–formaldehyde–water' system and, as a consequence, the choice of the predominant reaction route via the schemes (A) or (B) are regulated by both the concentration and the strength of acidic centers in applied zeolite catalyst. It is evident that the concentration in zeolite catalyst of strong protic centers of the type

$$\left[\begin{matrix} O \\ O \end{matrix}\!\!\!\!\searrow\!\! Al \cdot\cdot \overset{\ominus}{O}\!\!-\!\!Si\!\!\begin{matrix} O \\ O \end{matrix}\right] \left[H\right]^{\oplus}$$

is the factor, which specifies predominant reaction route and determines the final reaction product.

Acknowledgements

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