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# Aluminosilicates with different pores structure in the synthesis of 2,2,4-trimethyl-1,2-dihydroquinoline and *N*-phenyl-2-propanimine

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Physicochemical characteristics of microporous zeolites of various structural type (FAU, BEA, MTW), micro-meso-macroporous zeolite (H-Ymmm), and mesoporous aluminosilicate (ASM) were studied. Their catalytic activity in the reaction of aniline with acetone was examined. It was found that 2,2,4-trimethyl-1,2-dihydroquinoline was the main reaction product on the catalysts H-Ymmm and ASM (selectivity up to 68% at 100% conversion of aniline), while the reaction on zeolites with microporous structure mainly gave *N*-phenyl-2-propanimine (selectivity up to 91%).

**Key words:** dihydroquinolines, imines, zeolites, hierarchical zeolites, mesoporous aluminosilicates.

A dihydroquinoline ring is present in the structure of many natural and synthetic compounds possessing biological activity.[1,2] For example, compounds based on 2,2,4-substituted 1,2-dihydroquinolines exhibit antibacterial, antidiabetic and anti-inflammatory properties.[3—5] Apart from that, dihydroquinoline derivatives are inhibitors of lipid peroxidation and HMG-CoA-reductase, inhibitors of bile acid transporter, agonists and antagonists of progesterone.[6] Oligomers of 1,2-dihydroquinolines (di-, tri-, and tetramers) are also known as antioxidants of rubbers.[6]

1,2-Dihydroquinolines are commonly synthesized by the acid-catalyzed reaction of aromatic amines with ketones. This reaction is a modification af the classical Skraup method, according to which quinoline is obtained by heating aniline with glicerol in the presence of sulfuric acid.

Much work has been done on the synthesis of 2,2,4-trimethyl-1,2-dihydroquinoline (**1**) by the reaction of aniline with acetone in the presence of HCl, benzene- or *p*-toluenesulfonic acid, iron and copper chlorides.[6—9] Besides a multistep pathway, the main disadvantage of these methods is the formation of of alkylanilines and oligomers of dihydroquinoline **1** in large amounts.

There is a report[10] on the synthesis of 2,2-disubstituted 1,2-dihydro-4-phenylquinolines by the reaction of 2-(1-phenylvinyl)aniline and 4-chloro-2-(1-phenylvinyl)aniline with acetophenone derivatives in the presence of *p*-toluenesulfonic acid. The reaction of 2-isopropenylaniline with ketones in the presence of $BF_3 \cdot OEt$ afforded 2,2,4-trisubstituted 1,2-dihydroquinolines.[11]

A reaction of aromatic amines with ketones catalyzed by silicotungstic acid ($H_4[SiW_{12}O_{40}]$) in the presence of solvents was earlier described.[12] The yields of 1,2-dihydroquinolines varied within 77—94%. In recent works, the synthesis of dihydroquinolines **1** was carried out under the influence of microwave irradiation in the presence of triflates as efficient homogeneous catalysts (for example, $Sc(OTf)_3$, $In(OTf)_3$, and $Yb(OTf)_3$;[5] $Zn(OTf)_3$[13] or $Bi(OTf)$[14]). Compounds **1** were also obtained in the presence of cerium ammonium nitrate.[15]

Despite the high yields of dihydroquinolines **1**, the use of homogeneous catalysts has several disadvantages: a multistep pathway, difficulties in the removal of catalysts from the reaction mixture, the use of solvents in large amounts.

It should be noted that the use of heterogeneous catalysts in the synthesis of dihydroquinoline **1** has not been studied at length. For example, the gas-phase synthesis of 1,2-dihydroquinoline **1** affected by niobium halides ($[(Nb_6Cl_{12})Cl_2(H_2O)_4] \cdot 4H_2O$) proceeded with 71.1% selectivity at a 34% conversion of aniline.[16] A report[17] on the synthesis of dihydroquinoline **1** on polyhedral oligomeric silsesquioxanes was published. 1,2-Dihydroquinoline **1** was obtained in 96% yield by the reaction of aniline with acetone in the presence of natural aluminosilicate E4a.[18] The latter method is attractive due to the use of an environmentally friendly heterogeneous catalyst. However, its use in large amounts (250% calculated on aniline) significantly reduces the efficiency of the process. Apart from that, natural aluminosilicates are characterized by

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inconstancy of mineralogical and chemical composition, pore structure, strength and heat resistance indices, and other important characteristics. Natural zeolite materials contain such impurities as sand, clay minerals, and quartz. The composition and amount of metal cations present in natural zeolites can vary significantly.

Synthetic zeolites have not previously been used for the preparation of dihydroquinolines, therefore, it is of interest to study their catalytic properties in the reaction of aniline with acetone. As it is known, zeolites efficiently catalyze a variety of chemical processes. However, diffusion of reagent and reaction products through micropores is often retarded, resulting in a low activity of the catalyst and is rapid deactivation. Apart from that, the zeolite structure limits the possibility of synthesis of bulky molecules with a diameter more than 1 nm. Using mesoporous materials, it is possible to overcome the diffusion limitations characteristic of microporous systems and develop favorable conditions for the synthesis of bulky molecules.

In order to search for and develop efficient heterogeneous catalysts for the synthesis of dihydroquinolines by the reaction of aniline with acetone, in the present work we studied physicochemical and catalytic properties of microporous zeolites (H-Y, H-Beta, H-ZSM-12), the zeolite H-Ymmm with a combined micro-meso-macroporous structure, and an amorphous mesoporous aluminosilicate ASM.

## Experimental

**Reagents and catalysts.** Aniline and acetone distilled and purified according to the standard procedures[19] were used in the work.

The samples of zeolites $NH_4$-Beta ($SiO_2 : Al_2O_3 = 18$) and H-ZSM-12 ($SiO_2 : Al_2O_3 = 34$) were synthesized at the Angarsk Plant of Catalysts and Organic Synthesis Inc. Zeolite Beta obtained in the $NH_4$ form was converted to the H form by calcination during 4 h at 540 °C. Zeolite Na-Y ($SiO_2 : Al_2O_3 = 6$) was synthesized according to the known procedure[20] and converted to the H form by triple ion exchange in a solution of $NH_4NO_3$ at 70 °C to a decationization degree of $\alpha_{Na} = 0.96$. The preparation method for micro-meso-macroporous zeolite Ymmm in the H form ($SiO_2 : Al_2O_3 = 7.2$) is based on selective crystallization in solutions of sodium silicate at 96—98 °C of granules consisting of highly dispersed zeolite NaY and amorphous binder material (metakaolin).[21,22] With this method of preparation, the content of the crystalline phase in the sample is greater than that of the amorphous phase. The degree of exchange of $Na^+$ with $H^+$ ($\alpha_{Na}$) in the sample of H-Ymmm was 0.95. Amorphous mesoporous aluminosilicate ASM (Si : Al = 40) was obtained by sol—gel synthesis according to the procedure described earlier.[23,24]

Prior to catalytic tests, the catalysts were subjected to a high-temperature treatment (at 540 °C) in the atmosphere of dried air during 3—4 h.

**Methods of study of catalysts.** Methods for study of physicochemical properties of zeolite catalysts and mesoporous aluminosilicate are described in the literature.[23—25]

Acidic properties of aluminosilicates were studied by IR spectroscopy in the G. K. Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences using a low-temperature adsorption of the CO probe molecule.[26—30] IR spectra were recorded on a Shimadzu FTIR-8400 Fourier-transform spectrometer in the range of 700—6000 $cm^{-1}$ with a resolution of 4 $cm^{-1}$ and a number of scans equal to 250. Before experiments, the samples of catalysts were compressed into pellets with parameters $p/S \approx 0.009$—0.013 g $cm^{-2}$ (where $p$ is the pellet weight in g; $S$ is the pellet geometric area in $cm^2$).

**Synthesis of 2,2,4-trimethyl-1,2-dihydroquinoline (1) and *N*-phenyl-2-propanimine (2).** Aniline (0.1 g, 1 mmol), acetone (0.3 g, 5 mmol), and a catalyst (0.04 g, 10% calculated on the aniline—acetone mixture) were placed into a tube. The sealed tube was transferred into an autoclave, which was heated to 230 °C in a thermostatically controlled oven during 24 h with continuous rotation. After the reaction reached completion, the autoclave was cooled to ~20 °C, the tube was unsealed. The reaction mixture was filtered from the catalyst.

The reaction products were analyzed by GLC on a HRGS 5300 chromatograph (Carlo Erba) (a flame-ionizing detector, a 50 m×0.2 mm glass capillary column, an SE-30 phase, programmed heating 50—280 °C, carrier gas helium). Mass spectra were obtained on a SHIMADZU GCMS-QP2010Plus chromate-mass spectrometer (a SPB-5 phase, a 30 m×0.25 mm capillary column, carrier gas helium, programmed temperature 40—300 °C, the source of ions temperature 200 °C, ionization energy 70 eV). $^1H$ and $^{13}C$ NMR spectra of compounds in solution of $CDCl_3$ were recorded on a Bruker AVANCE-400 spectrometer (400.13 MHz (for $^1H$) and 100.62 MHz (for $^{13}C$)) in standard NMR tubes 5 mm in diameter.

**2,2,4-Trimethyl-1,2-dihydroquinoline (1).** The yield was 81.2%, a dark brown liquid, b.p. 75 °C (5 Torr), $n_D^{20}$ 1.521. $^1H$ NMR ($CDCl_3$), δ: 1.35 (s, 3 H, C(9,10), Me); 2.07 (d, 3 H, C(11), Me); 5.39 (d, 1 H, H(3)); 6.50 (d, 1 H, H(8), $J$ = 8 Hz); 6.72 (m, 1 H, H(7), $J$ = 4 Hz); 7.07 (m, 1 H, H(6), $J$ = 8 Hz); 7.15 (dd, 1 H, H(5), $J$ = 8 Hz). $^{13}C$ NMR ($CDCl_3$), δ: 18.66 (C(11)); 31.07 (C(9,10)); 51.85 (C(2)); 113.03 (C(8)); 117.21 (C(6)); 121.59 (C(4a)); 123.68 (C(7)); 128.44 (C(4), C(5)); 128.58 (C(3)); 143.33 (C(8a)). The data obtained correspond to the literature data.[18] MS (EI, 70 eV), $m/z$ ($I_{rel}$ (%)): 173 $[M]^+$ (13), 158 (100), 143 (12), 130 (6), 115 (17), 103 (2), 91 (5), 79 (9), 65 (6), 51 (4), 42 (1). Found (%): C, 83.21; H, 8.70; N, 8.07. $C_{12}H_{15}N$. Calculated (%): C, 83.01; H, 8.55; N, 8.00.

***N*-phenyl-2-propanimine (2).** The yield was 97%, a dark brown liquid, b.p. 35 °C (16 Torr), $n_D^{20}$ 1.490. $^1H$ NMR, δ: 1.84 (s, 6 H, C(9, 10), Me); 6.71—6.73 (dd, 2 H, C(2,6)H); 7.20 (t, 1 H, C(4)H); 7.73 (t, 2 H, C(3,5)H). $^{13}C$ NMR, δ: 20.62 (C(9,10)); 115.11 (C(2,6)); 123.13 (C(4)); 129.31 (C(3,5)); 146.47 (C(1)); 169.18 (C(8)). MS (EI, 70 eV), $m/z$ ($I_{rel}$ (%)): 133 $[M]^+$ (60), 118 (100), 103 (2), 93 (1), 77 (80), 59 (7), 51 (25), 41 (3). Found (%): C, 81.18; H, 8.30; N, 10.48. $C_9H_{11}N$. Calculated (%): C, 81.01; H, 8.21; N, 10.40.

## Results and Discussion

**Characteristics of catalysts**. Physicochemical properties of zeolites H-Y, H-Beta, H-ZSM-12, H-Ymmm and

**Table 1.** Physicochemical characteristics of zeolites

| Catalyst | $S_{BET}$ /m$^2$ g$^{-1}$ | $A^a$ / cm$^3$ g$^{-1}$ | | Acidic properties | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Lewis acid sites | | | | | | Brönsted acid sites | | |
| | | | | Strong$^b$ | | Medium$^c$ | | Weak$^d$ | | $\nu_{OH}$ | $\Delta\nu_{OH}{}^e$ | $N_H$ /μmol g$^{-1}$ |
| | | $H_2O$ | $C_6H_6$ | $N_{CO}{}^f$ | $Q_{CO}{}^g$ | $N_{CO}$ | $Q_{CO}$ | $N_{CO}$ | $Q_{CO}$ | cm$^{-1}$ | | |
| H-Y | 870 | 0.30 | 0.30 | 33 | 52 | — | — | 37 | 38 | 3610—3650 | 300 | 320 |
| | | | | | | | | | 3675 | 220 | 60 | |
| | | | | | | | | | 3675 | 163 | 73 | |
| H-Beta | 470 | 0.28 | 0.32 | 55 | 52 | 22 | 45 | 293 | 38 | 3613 | 324 | 128 |
| | | | | | | | | | | 3745 | 315 | 51 |
| H-ZSM-12 | 320 | 0.14 | 0.13 | 4 | 53 | 1 | 46 | 1 | 34 | 3621 | 330 | 75 |
| | | | | | | | | | | 3738 | 308 | 31 |
| H-Ymmm | 741 | 0.28 | 0.28 | 8 | 54 | 25 | 43—44.5 | 64 | 32.5—39 | 3600—3660 | 300—320 | 70 |
| | | | | | | | | | | 3735 | —$^h$ | 50 |
| ASM | 650 | — | — | 58 | 54.5—50.5 | 11 | 45—44 | 50 | 40—34 | 3615—3725 | 300 | 5 |
| | | | | | | | | | | 3740 | 270—320 | 23 |

[a] $A$ is the equilibrium adsorption capacity at 20 °C, $P/P_s = 0.8$.

[b] $\nu_{CO} = 2231—2226$ cm$^{-1}$;

[c] $\nu_{CO} = 2212—2210$ cm$^{-1}$;

[d] $\nu_{CO} = 2200—2190$ cm$^{-1}$;

[e] $\Delta\nu_{OH}$ is the shift of frequency of OH groups during adsorption of CO, cm$^{-1}$;

[f] $N_{CO}$ is the amount of adsorbed CO, μmol g $^{-1}$.

[g] $Q_{CO}$ is the heat of adsorption, kJ mol$^{-1}$;

[h] cannot by accurately measured.

amorphous mesoporous aluminosilicate ASM are given in Table 1.

According to the powder X-ray diffraction data and the adsorption capacity values for the $H_2O$ and $C_6H_6$ vapors, the samples of zeolites H-Y, H-Beta, and H-ZSM-12 are characterized by the degree of crystallinity close to 100%, while for zeolite H-Ymmm it is 95%. According to the low-temperature nitrogen adsorption—desorption data, the "apparent" BET specific surface area of zeolites is 870 (H-Y), 470 (H-Beta), 320 (H-ZSM-12), and 741 m$^2$ g$^{-1}$ (H-Ymmm). A hysteresis loop of type H 1 is observed on the nitrogen adsorption—desorption isotherm for zeolite H-Ymmm (Fig. 1), which is typical of micro-mesoporous structures.[31] A specific surface of the macropores of zeolite H-Ymmm determined by mercury porosimetry is equal to 12.1 m$^2$ g$^{-1}$. The volumes of micro-, meso-, and macropores are 0.28, 0.15, and 0.15 cm$^3$ g$^{-1}$, respectively.

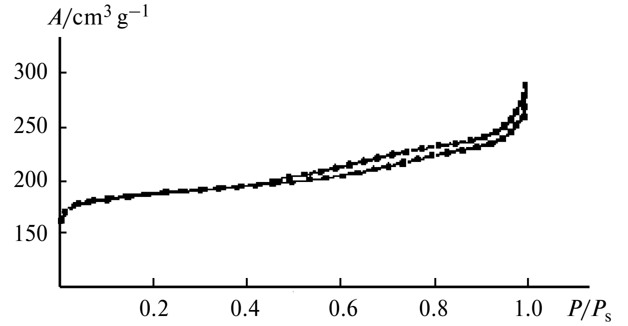


**Fig. 1.** Isotherm of nitrogen adsorption at 77 K for zeolite HY-mmm.

Acidic properties of the samples of zeolites and mesoporous aluminosilicate were studied by IR spectroscopy of the adsorbed CO. The vibrations of the OH groups present in the IR spectra of the samples of zeolite H-Y ($SiO_2 : Al_2O_3 = 6$) and zeolites H-Beta and H-ZSM-12 were interpreted earlier.[29,30] In zeolite H-Y, four types of Brönsted acid sites (BAS) are present, which are related to bridging Si—O(H)—Al groups in large cavities (absorption bands at 3610 and 3638 cm$^{-1}$), and two types of weakly acidic OH groups bonded to the out-of-lattice aluminum (absorption bands at 3675 cm$^{-1}$). The surface of the samples of zeolites H-Beta and H-ZSM-12 contain three types of BAS: the bridging OH groups in the channels characterized by the absorption bands at 3613 cm$^{-1}$ (H-Beta) and 3621 cm$^{-1}$ (H-ZSM-12); the bridging OH groups on the external surface of crystals, and weakly acidic terminal SiOH groups (absorption bands at 3738—3745 cm$^{-1}$). The values of the BAS concentrations and the $\Delta\nu_{OH}$ values of the shift of the absorption bands of the OH groups upon the formation of a hydrogen bond with CO are given in Table 1. The strength of the acid centers can be inferred from the $\Delta\nu_{OH}$ shift value: the larger is the shift value, the stronger is the acid site. According to the presented data, the concentration of BAS of microporous zeolites decreases in the order: H-Y > H-Beta > H-ZSM-12. The strength of BAS increases in the reverse order: H-Y < H-Beta < H-ZSM-12.

Apart from BAS, Lewis acid sites (LAS) of various strength were found on the surface of the zeolites: strong (most likely, dimeric Al—O—Al clusters, stabilized on Brönsted centers) and weak (apparently, clusters containing six—eight Al atoms and complexes of CO with nuclei of aluminum oxide phase), which are characterized by absorption bands at 2225—2230 and 2195—2187 $\mathrm{cm^{-1}}$, respectively.[26—28] The maximum amount of LAS (both in type and concentration) was found for the sample of zeolite H-Beta, namely, 370.3 $\mu\mathrm{mol\ g^{-1}}$.

The IR spectrum of the sample of micro-mesoporous zeolite H-Ymmm in the region of stretching vibrations of the OH groups is shown in Fig. 2, *a*.

The IR spectrum of the H-Ymmm sample exhibits absorption bands for nine types of hydroxy groups. A broad absorption band in the region of 3600 $\mathrm{cm^{-1}}$ is attributed to the vibrations of the OH groups in small zeolite cavities, these OH groups are not available for the adsorption of CO molecules. The absorption bands at 3610, 3630, and 3660 $\mathrm{cm^{-1}}$ can be assigned to strong bridging hydroxy groups Si—O(H)—Al in the zeolite cavities. The bands at 3680, 3690, and 3785 $\mathrm{cm^{-1}}$ belong to the OH groups bonded to the non-framework aluminum atoms (Al—OH).

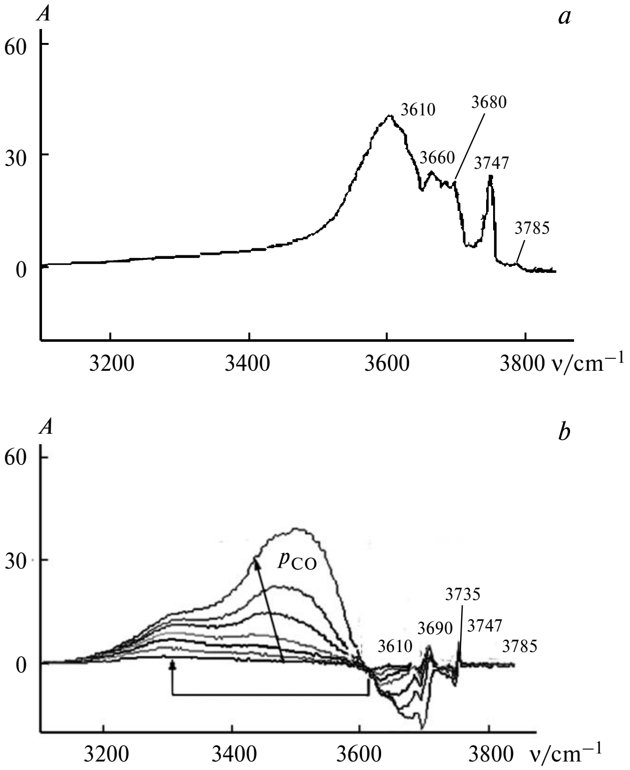


**Fig. 2.** IR spectra of the H-Ymmm sample in the region of vibrations of surface hydroxyl groups before adsorption (*a*) and difference spectra after adsorption of CO (0.2—4 Torr) at 77 K (*b*).

A signal in the region of 3735 $\mathrm{cm^{-1}}$ is related to the vibrations of strongly acidic Si—OH group on the external surface of zeolite crystallites, which are located in the immediate vicinity of the LAS formed by three-coordinated Al or Si atoms (Si—O(H)...$\mathrm{Al^{3+}}$ or Si—O(H)...$\mathrm{Si^{3+}}$). The band at 3747 $\mathrm{cm^{-1}}$ belongs to the terminal Si—OH groups.

The IR spectrum of the H-Ymmm sample in the region of vibrations of the OH groups after adsorption of CO is shown in Fig. 2, *b*. The shifts of the absorption bands of the OH groups upon formation of hydrogen bonds, the band frequency of the adsorbed CO, and the concentrations of acid sites are given in Table 1. It should be noted that the surface of the sample contains strong type I BAS ($\Delta\nu_{\mathrm{OH}}$ = 300 $\mathrm{cm^{-1}}$) related to the bridging Si—O(H)—Al groups and strong type II BAS related to the acid sites presumably on the external surface of the zeolite crystals with $\nu_{\mathrm{O-H}}$ = 3735 $\mathrm{cm^{-1}}$.

By estimating the amount of adsorbed CO on the surface of the H-Ymmm sample, the existence of three types of LAS can be assumed (see Table 1).

Comparing the acidic properties of the finely dispersed zeolite H-Y with the microporous structure and the granular zeolite H-Ymmm with the micro-meso-macroporous structure, it can be pointed out that zeolite H-Ymmm is characterized by a wider diversity of the OH groups. The concentration of strong BAS ($\Delta\nu_{\mathrm{OH}}$ = 300—320 $\mathrm{cm^{-1}}$) in zeolite H-Ymmm is considerably lower (120 $\mu\mathrm{mol\ g^{-1}}$) than in zeolite H-Y (320 $\mu\mathrm{mol\ g^{-1}}$), however, almost half of them are located on the external surface of the crystals. The amount of LAS in zeolite H-Ymmm is higher than in zeolite H-Y, though, the majority of them are sites of medium and weak strength.

The characteristics of mesoporous aluminosilicate ASM are presented in Table 1. More details on the texture and acidic properties of aluminosilicate ASM are given in an earlier published work.[24] The ASM sample is characterized by a narrow distribution of mesopores from 2 to 5 nm with a volume of 0.70 $\mathrm{cm^3\ g^{-1}}$. Two types of strong BAS are present on its surface: the bridging Si—O(H)—Al groups (absorption at 3615 $\mathrm{cm^{-1}}$) and Si—O(H)...$\mathrm{Al^{3+}}$ groups (absorption at 3730 $\mathrm{cm^{-1}}$) or Al—O(H)—Al groups (absorption at 3650 $\mathrm{cm^{-1}}$). Apart from that, the weakly acidic silanol groups are also present (absorption at 3740 $\mathrm{cm^{-1}}$). The total concentration of strong BAS is 28 $\mu\mathrm{mol\ g^{-1}}$, the total concentration of LAS is 119 $\mu\mathrm{mol\ g^{-1}}$.

**Reaction of aniline with acetone in the presence of zeolites with micro- and micro-meso-macroporous structure and mesoporous aluminosilicates.** The results of the investigation of the reaction of aniline with acetone in the presence of the H-Y, H-Beta, H-ZSM-12, H-Ymmm, and ASM samples are given in Table 2.

2,2,4-Trimethyl-1,2-dihydroquinoline (**1**) and *N*-phenyl-2-propanimine (**2**) are the main products of the reac-

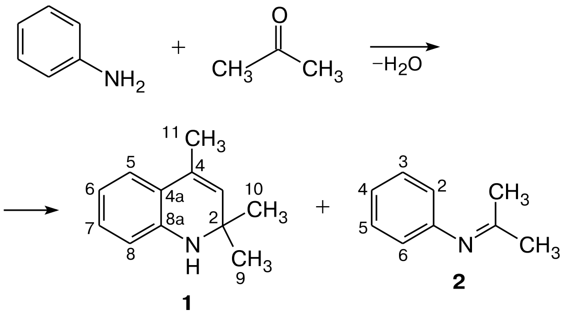
**Table 2.** The results of the reaction of aniline with acetone in the presence of zeolites with micro- and micro-meso-macroporous structure and mesoporous aluminosilicate*

| Catalyst | Conversion of aniline (%) | Selectivity of formation (%) | | |
|---|---|---|---|---|
| | | **1** | **2** | Other |
| H-Beta | 78 | 15 | 71 | 14 |
| H-ZSM-12 | 12 | 3 | 91 | 6 |
| H-Y | 11 | 7 | 88 | 5 |
| H-Ymmm | 100 | 68 | 30 | 2 |
| ASM | 85 | 49 | 47 | 4 |

* Synthesis conditions: the molar ratio of aniline : acetone = = 1 : 5; 10% of catalyst, 24 h, 230 °C.

tion of aniline with acetone in the presence of catalysts under study (Scheme 1).

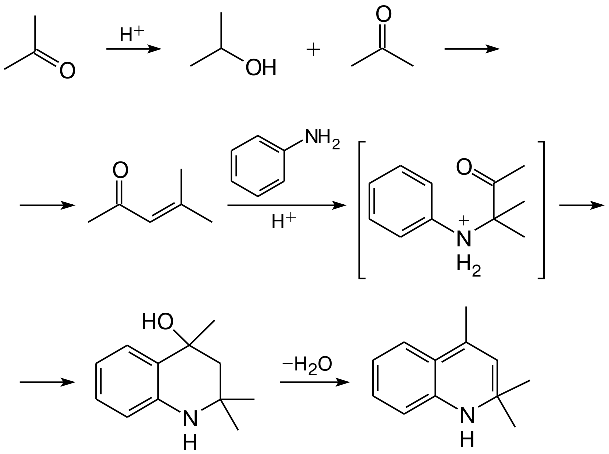
**Scheme 1**



**1** **2**

The activity of the catalysts in the reaction was evaluated from the degree of aniline conversion. Among zeolites with microporous structure, zeolite H-Beta exhibited a high activity in the reaction, while zeolites H-Y and H-ZSM-12 were found to be low active. From the comparison of the catalytic activity of zeolites with the data on their acidity (see Table 1), it follows that there is no correlation between the conversion of aniline and the concentration of acid sites on the catalysts, though, according to the assumed reaction mechanism, it should proceed with the involvement of the acid sites (Scheme 2). Thus, zeolite H-Y possessing the highest concentration of BAS has the lowest activity in the reaction (the conversion of aniline 11%), while on zeolite H-Beta, in which the amount of BAS is 2.5 times lower, the conversion of aniline reaches 78%. It should be noted that *N*-phenyl-2-propanimine (**2**) predominates in the reaction products obtained on microporous zeolites.

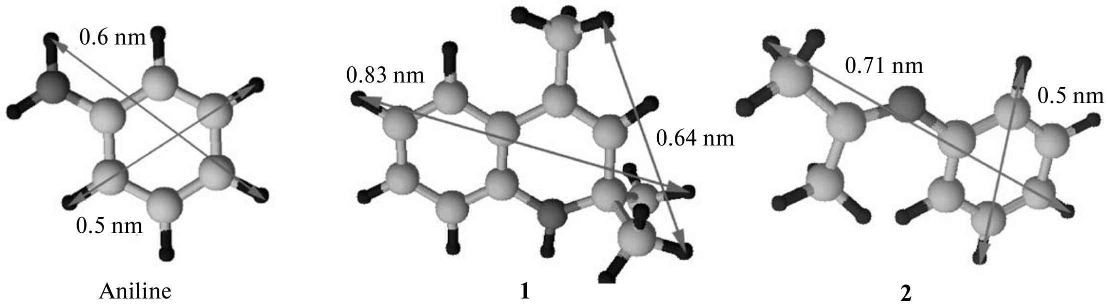
**Scheme 2**



The results obtained, namely, the absence of a correlation between activity and acidity and a selective formation of predominantly compound **2**, indicate a significant dependence of the catalytic properties on the textural characteristics of zeolites. Since in zeolites, as it is known, most of the active sites (strongly acidic structural OH groups) are located inside channels or cavities, it is their availability for the reacting molecules that is the main factor determining the catalytic properties.

The calculations by the ACD/3D Viewer program show that the sizes of the molecules of the parent compounds and reaction products **1** and **2** are close to or even exceed the diameter of the channels and cavities of the zeolites (Fig. 3).

Dihydroquinoline **1** has the bulkiest molecule with a size of 0.64×0.83 nm, the synthesis of which in micropores of the zeolite lattice is difficult and apparently possible



Aniline **1** **2**

**Fig. 3.** Sizes of molecules of aniline and reaction products **1** and **2**.

only on acid sites located on the external surface of the catalyst. The selectivity of the formation of dihydroquinoline **1** on zeolite H-Beta, that is higher than that observed on other zeolites, is due to the presence of strong BAS on the external surface of this zeolite (551 μmol $g^{-1}$, $\Delta\nu_{OH}$ = 315 $cm^{-1}$, see Table 1). It is obvious that the same reason explains the high catalytic activity of zeolite H-Beta, especially since the presence of a maximum amount of LAS (370 μmol $g^{-1}$), located mainly on the external surface of the crystals, is typical of zeolite H-Beta. It is believed[32] that the role of LAS consists in the increase in proton acidity effected by pulling the electron density away from the O—H bond. Apart from that, the reaction medium contains water formed in the course of the reaction. The dissociation of water molecules coordinatively bound to LAS can result in the appearance of new BAS.[33] Taking into account these suggestions, one can conclude that there is much more BAS on zeolite H-Beta than it was determined by IR spectroscopy, which explains a high catalytic activity of this zeolite.

A low activity of zeolite H-ZSM-12 is associated with considerable difficulties for the diffusion of the molecules of reagents and imine **2** caused by its crystal lattice with a diameter of channels of 0.53×0.56 nm and 0.51×0.55 nm.[34] The reason for the low activity of zeolite H-Y can not only be sought in steric hindrance for the diffusion and interaction of reagents. The blocking of large cavities by the formed molecules of dihydroquinoline **1** can be also considered when one bears in mind that the diameter of the entrance windows to a large cavity is smaller than the diameter of the cavity itself (0.75 and 1.2 nm, respectively).[34]

One way to improve the diffusion properties of zeolites and increase the availability of their active sites for reacting molecules is the creation of mesopores in their microcrystalline lattice. Various methods can be used to develop the mesoporosity in zeolite, for example, by means of templates, chemical or steam treatment.[35,36] In the present study, we used a granular zeolite H-Ymmm, in the porous structure of which micropores of primary crystals ($d$ = 0.75 nm) are present along with meso- (2—50 nm) and macropores (100—1000 nm) formed as a result of the formation of intergrowths of crystals in the process of the synthesis of granules of high degree of crystallinity.

As can be expected, the zeolite-based catalyst with a combined micro-mesoporous structure exhibits a higher activity than the catalysts with a microporous structure (see Table 2). Apart from that, the appearance of mesoporosity in zeolite significantly affects the selectivity of its action. In contrast to microporous zeolites, dihydroquinoline **1** becomes the main product of the reaction of aniline with acetone in the presence of zeolite H-Ymmm.

Aluminosilicate ASM was also studied as a catalyst with a mesoporous structure in the reaction of aniline with acetone (see Table 2). It was found that the amorphous aluminosilicate ASM exhibited a lower activity compared to that of zeolite H-Ymmm: the aniline conversion was 85% under the conditions used. This is likely due to a lower concentration of acid sites present on the surface of aluminosilicate ASM (see Table 1). The selectivity of the formation of imine **2** and dihydroquinoline **1** is approximately the same.

In conclusion, the present study revealed the relationship between the acid properties and characteristics of the porous structure of various zeolite catalysts and mesoporous aluminosilicate with their activity and selectivity in the cyclocondensation reaction of aniline with acetone. It was found that the main product of the reaction of aniline with acetone in the presence of microporous zeolite catalysts is *N*-phenyl-2-propanimine (**2**), which is explained by the molecular-sieve effect of the zeolite crystal lattice. 1,2-Dihydroquinoline (**1**) is most selectively formed on the micro-mesoporous zeolite H-Ymmm (68%), the selectivity of the formation of compound **1** decreases to 49% on the mesoporous aluminosilicate ASM. The presence of mesopores in the aluminosilicates described above contributes to the reduction of steric hindrance for the transport of reagents and development of conditions for the formation of compound **1**. The activity of the catalysts decreases in the following order: H-Ymmm (100% conversion of aniline) > ASM (85%) > > H-Beta (78%) > H-ZSM-12 (12%) > H-Y (11%).

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