Aluminosilicates with Different Porous Structures in the Synthesis of 2-Ethyl-3-Methylquinoline

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Abstract—The catalytic properties of microporous zeolites of different structural types (FAU, BEA, MOR, and MFI), a micro—meso—macroporous zeolite (H-Ymmm), and an ASM mesoporous aluminosilicate in the reaction of aniline with propionic aldehyde have been studied. It has been found that the reaction proceeds with a high conversion of aniline (90-99% over zeolites and 71% over an ASM aluminosilicate) to form two main products, namely, 2-ethyl-3-methylquinoline (2) and 2-ethyl-3-methyl-*N*-phenyl-1,2,3,4-tetra-hydroquinoline-4-amine (3). The most selective catalysts for the synthesis of quinoline 2 are H-Y (up to 64%) and H-Ymmm (59%) zeolites and the ASM aluminosilicate (50%). It has been shown that an increase in the quinoline 2 selectivity is promoted by an increase in the catalyst acidity, in the reaction temperature to 160°C, in the catalyst concentration to 20 wt %, and in the aniline : aldehyde molar ratio to 1 : 2.

Keywords: quinolines, 1,2,3,4-tetrahydroquinolines, aniline, aldehydes, condensation, zeolites, hierarchal zeolites, mesoporous aluminosilicates

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Quinoline and its derivatives are widely used for the production of highly efficient medicines possessing antibacterial, fungicidal, antiparasitic, and antineoplastic activities [1-3]. Corrosion inhibitors, preserving agents, resin solvents, refinery defoamers [4], and luminescent materials [5] are produced on the basis of quinolines.

Various methods have been proposed for the synthesis of quinolines, namely, Skraup, Knorr, Doebner–Miller, Friedländer, Combes, Pfitzinger, and Conrad–Limpach [6]; however, most of them are characterized by the use of acids or bases as catalysts, multistage nature, harsh reaction conditions, and low yields. The preparation of 2-ethyl-3-methylquinoline **2** (yield, 59%) from aniline and propionic aldehyde in the presence of the metal complex catalyst [Rh(norbornadiene)Cl]₂ is known [7].

Works, in which zeolites were used for the synthesis of quinoline derivatives, are still scarce [8, 9]. Thus, the synthesis of 2- and 4-methylquinolines via the reaction of aniline with acetaldehyde over H-Beta zeolite with an overall yield of 83% was reported [9]. Guo et al. [10] developed a method for the synthesis of substituted alkylquinolines in a yield of 29–81% from arylamines and aldehydes over a mesoporous MCM-41/Cp₂ZrCl₂ material.

In this connection, the search for and development of highly efficient heterogeneous catalysts and methods for the synthesis of alkylquinolines on their basis are important and relevant tasks.

In this paper we present the results of the investigation of the activity and selectivity of various crystalline and amorphous aluminosilicates differing in texture, porosity, and acid properties, namely, microporous zeolites (H-Y, H-Beta, H-MOR, and H-ZSM-5), a H-Ymmm micro-meso-macroporous zeolite, as well as an ASM mesoporous aluminosilicate in the synthesis of 2-ethyl-3-methylquinoline **2** via the reaction of aniline with propionic aldehyde.

EXPERIMENTAL

Chemicals and Catalysts

Aniline (99.8 wt %) and propionic aldehyde (97 wt %) (Acros) were used in this study.

Zeolites of the FAU (H-Y and H-Ymmm), BEA (H-Beta), MFI (H-ZSM-5), and mordenite (H-MOR) structural types and an ASM amorphous mesoporous aluminosilicate were investigated as the catalysts.

Zeolite Na-Y (SiO₂/Al₂O₃ = 5.0) was synthesized according to a procedure described in [11] and con-

verted into the H-form by triple ion exchange in a solution of NH_4NO_3 at 70°C to the degree of decationation of $\alpha_{Na} = 0.80$. Samples of H-Beta $(SiO_2/Al_2O_3 = 40)$ and H-ZSM-5 $(SiO_2/Al_2O_3 = 50)$ zeolites were prepared using ion exchange of Na⁺ cat-

ions to NH_4^+ cations in the samples of Na-Beta and Na-ZSM-5 (Zeolyst) followed by the thermal treatment of the obtained ammonium form. A Na-MOR zeolite (SiO₂/Al₂O₃ = 10.0) was synthesized according to a procedure described in [12] and transformed to

the H-form using ion exchange of Na^+ cations to NH_4^+ cations followed by the thermal treatment of the obtained ammonium form.

The procedure for preparing Ymmm micromeso-macroporous zeolite in the H-form $(SiO_2/Al_2O_3 = 7.2)$ is described in [13] and is based on the selective crystallization of granules consisting of finely divided Na-Y zeolite and amorphous binder (metakaolin) in sodium silicate solutions at 96–98°C. Samples of H-Ymmm zeolites with α_{Na} of 0.5, 0.6, 0.75, and 0.95 were prepared using ion exchange of a sample of Na-Ymmm; hereinafter, these samples are denoted as 0.5H-Ymmm, 0.6H-Ymmm, 0.75H-Ymmm, and 0.95H-Ymmm.

The amorphous mesoporous aluminosilicate ASM $(SiO_2/Al_2O_3 = 20)$ was obtained via sol-gel synthesis according to a procedure described in [14, 15].

Prior to catalytic tests, the catalysts were subjected to high-temperature treatment in a dry air atmosphere at 540° C for 3 to 4 h.

Catalyst Investigation Methods

To study the physicochemical properties of the prepared samples of zeolites and mesoporous aluminosilicate, X-ray fluorescent, X-ray phase, and X-ray structural analyses, ²⁷Al MAS NMR spectroscopy, scanning electron microscopy, low-temperature adsorption–desorption of nitrogen, and temperatureprogrammed desorption of ammonia (TPD-NH₃) were used. Methods for the investigation of the physicochemical properties of the studied zeolite catalysts are described in [13, 16], and the mesoporous aluminosilicate, in [14, 15].

Synthesis of N-Propylaniline, 2-Ethyl-3-Methylquinoline, and 2-Ethyl-3-Methyl-N-Phenyl-1,2,3,4-Tetrahydroquinoline-4-Amine

A metal autoclave was charged with 0.25 mL (2.8 mmol) of aniline and then 0.20–0.60 mL (2.8–8.4 mmol) of propionic aldehyde depending on the required molar ratio, 1 mL of chlorobenzene, and the test catalyst in an amount of 10-50% of weight of the reactant mixture; tightly sealed; and placed into a thermostated cabinet. The reaction was carried out at $25-200^{\circ}$ C for 6 h with continuous rotation of the

autoclave. Upon completion of the reaction, the reaction mixture was cooled to room temperature, the catalyst was filtered off, and the residue was chromatographed on a SiO₂ column (the eluent is hexane \rightarrow hexane–ethyl acetate blend).

The GLC analysis of the products was performed on a Shimadzu GC-9A chromatograph with a flame ionization detector, a 3-m packed column, the SE-30 phase, programming at 50–250°C, and helium as the carrier gas.

The ¹H and ¹³C NMR spectra in the COSY, HSQC, and HMBC homo- and heteronuclear modes were recorded on Bruker Avance-400 (operating frequency of 400.13 MHz for ¹H and 100.62 MHz for ¹³C) and Bruker Avance III 500 HD Ascend (operating frequency of 500.17 MHz for ¹H and 125.78 MHz for ¹³C) instruments; the solvent was CDCl₃.

N-**Propylaniline (1).** Yield 2–11% depending on the catalyst type. An oily yellow liquid. $T_{\rm b}$ 96°C/10 mmHg. ¹H NMR spectrum (500.17 MHz, CDCl₃, δ , ppm): 1.04 (t, J = 7.3 Hz, 3H), 1.69 (m, 2H), 3.12 (t, J = 7.0 Hz, 1H), 6.70 (d, J = 7.5 Hz, 2H), 6.73 (t, J = 7.3 Hz, 1H), 7.21 (t, J = 7.8 Hz, 2H). ¹³C NMR spectrum (125.78 MHz, CDCl₃, δ , ppm): 11.67, 22.75, 45.83, 112.73, 117.11, 129.24, 129.41, 148.52. The obtained data correspond to the published data [17].

2-Ethyl-3-methylquinoline (2). Yield 23–62% depending on the catalyst type. An oily yellow liquid. $T_{\rm b}$ 97–99°C/2 mmHg. ¹H NMR spectrum (500.17 MHz, CDCl₃, δ , ppm): 1.41 (t, J = 7.5 Hz, 3H), 2.48 (s, 3H), 3.01 (quartet, J = 7.5 Hz, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.62 (t, J = 8.0 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.81 (s, 1H), 8.06 (d, J = 8.5 Hz, 1H). ¹³C NMR spectrum (125.78 MHz, CDCl₃, δ , ppm): 12.86, 19.11, 29.51, 125.61, 126.71, 127.34, 128.30, 128.54, 129.41, 135.75, 146.67, 163.28. The obtained data correspond to the published data [18].

2-Ethyl-3-methyl-*N***-phenyl-1,2,3,4-tetrahydro-quinoline-4-amine (3).** Yield 5–34% depending on the catalyst type. Transparent crystals. $T_{\rm m}$ 104–106°C. ¹H NMR spectrum (500.17 MHz, CDCl₃, δ , ppm): 1.01 (t, *J* = 9.5 Hz, 3H), 1.11 (d, *J* = 8.5 Hz, 3H), 1.61– 1.67 (m, 2H), 1.88–1.94 (m, 1H), 3.14–3.18 (m, 1H), 3.85 (br. s, 2H), 4.34 (d, *J* = 11.5 Hz, 1H), 6.55 (d, *J* = 10.0 Hz, 2H), 6.62–6.77 (m, 2H), 7.06 (t, *J* = 8.8 Hz, 1H), 7.19–7.27 (m, 4H). ¹³C NMR spectrum (125.78 MHz, CDCl₃, δ , ppm): 9.12, 15.76, 26.49, 37.39, 56.44, 57.86, 112.50, 113.25, 113.86, 116.85, 117.36, 123.38, 128.05, 128.31, 129.40, 129.45, 144.37, 148.76.

Catalyst	Crystallinity, rel. %	$S_{\rm BET},{\rm m^2/g}$	Equilibrium adsorption capacity (20°C and $P/P_s = 0.8$), cm ³ /g, for vapors of		Acid properties		
					concentration of acid sites, μ mol g ^{-1*}		
			H ₂ O	C_6H_6	C_{I}	C_{II}	С
H-Y	100	870	0.30	0.30	610	520	1130
H-Beta	100	625	0.12	0.32	520	310	830
H-MOR	100	393	0.18	0.16	651	349	1000
H-ZSM-5	100	360	0.14	0.15	270	190	460
0.5H-Ymmm	93	_	0.30	0.30	450	340	790
0.6H-Ymmm	93	_	0.29	0.30	460	390	850
0.75H-Ymmm	93	_	0.29	0.31	480	410	890
0.95H-Ymmm	93	741	0.25	0.30	515	460	975
ASM	0	640	_	_	350	120	470

 Table 1. Physicochemical characteristics of the catalysts

 $* C_{I}, C_{II}$, and C are the concentrations of weak and strong acid sites and the total concentration, respectively.

RESULTS AND DISCUSSION

Catalyst Characterization

The physicochemical properties of the studied H-Y, H-Beta, H-ZSM-5, H-MOR, and H-Ymmm zeolites with different α_{Na} values and the ASM mesoporous aluminosilicate are presented in Table 1.

According to the XRD data and values of the adsorption capacity for H_2O and C_6H_6 vapors, H-Y, H-Beta, H-MOR, and H-ZSM-5 zeolites are characterized by crystallinity close to 100% whereas for the H-Ymmm zeolite samples have a crystallinity of 93%, which is explained by the partial crystallization of its amorphous component.

According to the data of low-temperature adsorption-desorption of nitrogen, the "apparent" BET specific surface area of the zeolites is 870 (H-Y), 625 (H-Beta), 360 (H-ZSM-5), 393 (H-MOR), or 741 (H-Ymmm) m²/g (Table 1). The specific surface area of H-Ymmm zeolite macropores determined using mercury porosimetry is 12.1 m²/g. The micro-, meso-, and macropore volumes are 0.28, 0.15, and 0.15 cm³/g, respectively.

Detailed information about the texture and acid properties of the ASM aluminosilicate is set forth in [15]. Note that the ASM sample is characterized by narrow distribution of mesopores from 2 to 5 nm with a volume of $0.70 \text{ cm}^3/\text{g}$.

The acid properties of the samples of the zeolites and a mesoporous aluminosilicate were studied by TPD-NH₃. Two peaks are observed in the TPD-NH₃ spectra of the microporous zeolites, namely, a low-temperature peak with a maximum at $250-300^{\circ}$ C and a high-temperature peak with a maximum in the range of 410- 480° C. This gives evidence for the presence of two types of acid sites, namely, weak sites that are characterized by a low-temperature peak and strong sites characterized by a high-temperature peak, in the samples under study [19]. In the series of microporous zeolites, the concentration of strong acid sites, which are the most important for catalytic transformations, decreases in the following order: H-Y > H-MOR > H-Beta > H-ZSM-5. The total concentration of acid sites changes in a similar manner.

There are two peaks in the acidity spectra of the samples of a H-Ymmm zeolite, which characterize weak acid sites with a temperature maximum in the temperature range of 250–280°C and strong acid sites at temperatures of 350–420°C. The concentration of strong acid sites in the H-Ymmm zeolite increases with an increase in the degree of decationation.

According to the data presented in Table 1, the mesoporous aluminosilicate ASM possesses the lowest acidity among the studied catalysts because (a) it contains the smallest number of strong acid sites (they are generally responsible for the occurrence of reactions) and (b) the strength of the specified acid sites is lower compared to the zeolites, as evidenced by the shift of the high-temperature peak to lower temperatures.

Catalytic Properties of the Zeolites and the Mesoporous Aluminosilicate in the Reaction of Aniline with Propionic Aldehyde

It has been found that the main products of the reaction of aniline with propionic aldehyde in the presence of the studied catalysts are 2-ethyl-3-methylquinoline **2** and 2-ethyl-3-methyl-*N*-phenyl-1,2,3,4-tetrahydroquinoline-4-amine **3** (Scheme 1). In addition to them, *N*-propylaniline **1**, condensation products of propionic aldehyde, and 2,3-dialkyldihydroquinoline were identified in the reaction mass. In Table 2 that presents the results of the investigation of the catalytic properties of the zeolites and a mesoporous aluminosilicate, all the reaction products except for compounds **1**–**3** are summarized and denoted as "others".

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catalyst	conversion	selectivity of formation, %					
Catalyst	of aniline, %	1	2	3	Others		
H-Y	97	5	64	15	16		
H-Beta	99	2	46	20	32		
H-MOR	99	1	32	34	33		
H-ZSM-5	90	7	39	28	26		
0.95H-Ymmm	95	4	59	14	23		
ASM	71	15	50	7	28		

Table 2. Reaction of aniline with propionic aldehyde in the presence of zeolites and mesoporous aluminosilicate

catalyst	conversion	selectivity of formation, %				
Catalyst	of aniline, %	1	2	3	Others	
H-Y	97	5	64	15	16	
H-Beta	99	2	46	20	32	
H-MOR	99	1	32	34	33	
H-ZSM-5	90	7	39	28	26	
0.95H-Ymmm	95	4	59	14	23	
ASM	71	15	50	7	28	

Synthesis conditions: molar ratio aniline : aldehvde = 1 : 2, 20 wt % catalyst. 160° C, the solvent is chlorobenzene. 6 h



Scheme 1. The reaction of aniline with propionic aldehyde.

The product composition indicates that in the case of aniline reaction with propionic aldehyde, the reactions of linear homo- and heterocondensation, cyclocondensation, dimerization, rearrangement, etc. proceed simultaneously. The presence of tetrahydroquinoline 3 among the products confirms the 2-ethyl-3methylquinoline formation mechanism proposed in [20] and depicted in Scheme 2. According to this mechanism, the interaction of aniline with the aldehyde proceeds through Schiff base (4) which is then transformed to N-propylamine 1 and dimer (5). The latter forms a complex with the catalyst (6), from which compound (7) is produced as a result of intramolecular cyclization. The subsequent reductive elimination of the catalyst in compound 7 leads to tetrahydroquinoline 3, which transforms into desired dialkylquinoline 2 as a result of elimination of aniline.



Scheme 2. The proposed mechanism of formation of 2-ethyl-3-methylquinoline 2.

The reaction of aniline with propionic aldehyde in the presence of all the zeolite catalysts studied proceeds with a high aniline conversion (Table 2), which is almost complete over H-Y. H-Beta, and H-MOR zeolites and is somewhat lower (90-95%) over H-ZSM-5 and H-Ymmm zeolites. The lowest conversion of aniline (71%) was observed over the ASM mesoporous aluminosilicate, which is apparently due to the low acidity of this catalyst.

Dialkylquinoline 2 is the most selectively formed over H-Y and H-Ymmm zeolites (64% and 59%, respectively). The mesoporous aluminosilicate ASM has selectivity (50%) close to that of the aforementioned zeolites. The other catalysts were less selective

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Fig. 1. The influence of the degree of decationation α_{Na} of a H-Ymmm zeolite on the conversion of aniline and the product composition. The catalyst is (A) H-Y, (B) 0.5H-Ymmm, (C) 0.6H-Ymmm, (D) 0.75H-Ymmm, and (E) 0.95H-Ymmm. Synthesis conditions: aniline : aldehyde molar ratio = 1 : 2, 20 wt % catalyst, 160°C, the solvent chlorobenzene, 6 h.

for dialkylquinoline **2**. A mixture of dialkylquinoline **2** and tetrahydroquinoline **3** in a ~ 1 : 1 ratio was obtained over the H-MOR zeolite, which exhibited the lowest dialkylquinoline **2** selectivity.

The difference in selectivity for quinoline 2 between the catalysts is presumably due to the differences in their porous structure. Quinoline 2 is formed most selectively over wide-pore catalysts, namely, the H-Y zeolite possessing the greatest diameter of the entrance windows in the series of the tested zeolite catalvsts: the H-Ymmm zeolite, the microporous structure of which is combined with meso- and macropores; and the ASM amorphous mesoporous aluminos-The low selectivity for quinoline 2 ilicate. demonstrated by H-MOR and H-ZSM-5 zeolites is apparently associated with the structural characteristics of their crystal lattice as well. The H-MOR zeolite has a unidimensional channel structure rather than a three-dimensional structure like the other catalysts studied. This characteristic feature of the H-MOR zeolite, as well as the presence of narrow tortuous channels in the H-ZSM-5 zeolite lattice, can lead to the complication of the diffusion of reactant and product molecules inside the zeolite crystalline framework.

Since the catalytic properties of zeolites in the Hform are associated with the presence of acid sites in their cavities and channels, it was of interest to study the influence of the concentration of acid sites of the samples on their activity and selectivity in the reaction of aniline with propionic aldehyde (Fig. 1). It has been shown by the example of four H-Ymmm zeolite samples differing in the degree of exchange of Na⁺ for H⁺ ions ($\alpha_{Na} = 0.5, 0.6, 0.75, and 0.95$) that under the studied conditions, the conversion of aniline little depends on α_{Na} and is high (93–95%) over all the samples. The concentration of quinoline **2** in the reaction products increases (from 25 to 59%) with the increase in α_{Na} , and the concentration of tetrahydroquinoline 3 decreases. Such a character of change in the concentration of 3 confirms that it is intermediate in the course of formation of quinoline 2. With the increase in α_{Na} , the concentration of the acid sites in the H-Ymmm zeolite increases (Table 1); therefore, a higher concentration of acid sites is required for more complete transformation of tetrahydroquinoline 3 to quinoline 2.

Based on this, the low selectivity for quinoline 2 in the presence of the H-MOR zeolite possessing a quite high concentration of acid sites can be explained by the inaccessibility of the active sites inside the channels for the bulky molecules of tetrahydroquinoline 3 and the occurrence of the reaction mainly over weaker surface active sites.

The influence of temperature, molar ratio of the reactants, and catalyst concentration on the aniline conversion of and selectivity for the products was studied using the 0.95H-Ymmm zeolite as an example.

The reaction of aniline with propionic aldehyde intensely occurs already at 20°C (Fig. 2), with the selectivity for quinoline **2** being 40% and tetrahydroquinoline **3** appearing in a significant amount (28%) in the reaction mixture. Increasing the temperature from 20 to 180°C leads to an increase in the conversion of aniline and a growth in the quinoline **2** selectivity, with the concentration of tetrahydroquinoline **3** decreasing to 9%.

The study of the influence of the catalyst concentration has shown that quinoline 2 is the most selectively formed in the presence of 20% H-Ymmm zeolite (Fig. 3). Both a decrease in the amount of the catalyst to 10% and its increase to 50% lead to a decrease in the quinoline 2 selectivity. The conversion of aniline in the studied range of catalyst concentrations is 92-97%.



Fig. 2. The influence of the reaction temperature on the yield and composition of the products. Synthesis conditions: aniline : aldehyde = molar ratio 1 : 2, 20 wt % catalyst, the solvent chlorobenzene, 6 h.



Fig. 3. The influence of the concentration of the catalyst on the yield and composition of the products. Synthesis conditions: aniline : aldehyde molar ratio = $1 : 2, 160^{\circ}$ C, the solvent chlorobenzene, 6 h.

Increasing the aniline : aldehyde molar ratio from equimolar to 1 : 3 leads to an increase in the aniline conversion (89-97%); however, a large excess of the aldehyde promotes the formation of propanal condensation products, so that the selectivity for the target quinolines decreases. The optimum aniline : aldehyde ratio is 1 : 2 (Fig. 4).

In summary, the study has revealed as a result an interrelation of the acid properties and characteristics of the porous structure of various zeolite catalysts having microporous (H-Y, H-Beta, H-MOR, and H-ZSM-5) and hierarchal (H-Ymmm) structures and the amorphous mesoporous aluminosilicate ASM with their activity and selectivity in the cycloconden-

sation reaction of aniline with propionic aldehyde. It has been found that 2-ethyl-3-methylquinoline **2** and 2-ethyl-3-methyl-*N*-phenyl-1,2,3,4-tetrahydroquinoline-4-amine **3** are the main products in the presence of the test catalysts. 2-Ethyl-3-methylquinoline **2** is the most selectively formed over wide-pore catalysts, namely, the H-Y zeolite (64% at an aniline conversion of 97%), the micro-meso-macroporous zeolite H-Ymmm (59% at an aniline conversion of 95%), and the mesoporous aluminosilicate ASM (50% at an aniline conversion of 71%). Tetrahydroquinoline-4amine **3** formed converts into quinoline **2** during the course of the reaction. The open three-dimensional system of wide-pore channels or cavities, the presence



Fig. 4. The influence of the molar ratio of reactants on the yield and composition of the products. Synthesis conditions: 20 wt % H-Ymmm catalyst, 160°C, the solvent chlorobenzene, 6 h.

of meso- and macropores, and an increase in the concentration of acid sites facilitate this process over zeolite catalysts. The conditions found for producing 2ethyl-3-methylquinoline **2** over the H-Ymmm zeolite with the maximum yield are as follows: the aniline : aldehyde molar ratio of 1 : 2, 20 wt % catalyst, 160° C, chlorobenzene as the solvent, 6 h.

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