

## Mesoporous Aluminosilicates in the Synthesis of *N*-Heterocyclic Compounds

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Received August 9, 2018; revised October 15, 2018; accepted December 19, 2018

**Abstract**—The catalytic properties of samples of amorphous mesoporous aluminosilicate ASM with different Si/Al molar ratios (40, 80, 160) were studied in the synthesis of practically important pyridines (by the interaction of C<sub>2</sub>–C<sub>5</sub> alcohols with formaldehyde and ammonia, cyclocondensation of acetaldehyde and propionic aldehyde with ammonia), dialkylquinolines and alkyltetrahydroquinolines (by reaction of aniline with C<sub>3</sub>, C<sub>4</sub> aldehydes) and alkyldihydroquinolines (by interaction of aniline with ketones, acetone and acetophenone). It is found that mesoporous aluminosilicate ASM sample with a molar ratio of Si/Al = 40, which has the highest acidity among the studied samples, exhibits the highest activity and selectivity in these reactions.

**Keywords:** mesoporous aluminosilicate ASM, cyclocondensation with ammonia/amines, pyridines, quinolines, hydroquinolines, tetrahydroquinolines

**DOI:** 10.1134/S0023158419020022

### INTRODUCTION

Nitrogen-containing heterocyclic compounds are a broad class of organic substances, many of which are of practical importance. Pyridines and quinolines are among the demanded. Polymer, chemical, pharmaceutical and other industries are consumers of pyridines. Over 150 years after the discovery of pyridine, hundreds of effective medicines have been found and synthesized [1], and the search for new forms of the pyridine compounds continues [2–4]. Alkylpyridines, specifically,  $\alpha$ -picoline (2-methylpyridine),  $\gamma$ -picoline (4-methylpyridine), and 5-ethyl-2-methylpyridine, are used as a raw material for the production of 2-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine, on the basis of which latexes for tire cord impregnation, ion exchange resins, and photographic materials are made [5–7]. Alkylpyridines are also raw materials for the production of chemical plant protection products against weeds, pests, and various diseases [8, 9]. Extractants, inhibitors of metal corrosion, solvents, surfactants, rubber vulcanization accelerators, and other products were synthesized on the basis of substituted pyridines [9–12].

Quinoline derivatives are important intermediates in the synthesis of biologically active compounds and herbicides [13]. A number of antimalarial [14, 15], antibacterial, antiseptic, antituberculous drugs [16],

anticancer drugs [17] prepared on the basis of quinolines are known. The quinoline fragment is found in some widely used antibiotics [18].

Many methods have been developed for the synthesis of both pyridines and quinolines. Industrially important methods for producing *N*-heterocyclic compounds consist mainly in the condensation of various carbonyl compounds with ammonia or amines under the action of acids or bases [19]. These processes are characterized by the formation of a significant amount of by-products. The target products are formed unselectively, therefore the creation of highly selective heterogeneous catalytic methods for the production of *N*-heterocyclic compounds is an important and topical task.

In recent years, zeolite catalysts have been actively used for the synthesis of *N*-heterocyclic compounds [20], which provide many advantages in the conversion of harmful environmentally hazardous cyclocondensation processes of carbonyl compounds with ammonia into green chemical production. However, it should be noted that the significant disadvantages of zeolites is their rapid deactivation due to the blocking of the micropores of the crystal lattice by the reaction products and coke. In addition, the microporous structure of the zeolite limits or hinders the synthesis

of bulk molecules with a diameter of about 1 nm or greater.

A new approach to the heterogeneous catalytic synthesis of *N*-heterocyclic compounds is the use of mesoporous materials as catalysts, which, as we assumed, will reduce transport difficulties for the movement of bulk molecules of reactants and reaction products. Moreover, in the mesopores, the concentration of the reacting molecules may be higher, which will lead to an increase in the number of chemical interaction acts of the reactants and an increase in the degree of their conversion. For such bulky molecules as alkyl(aryl)quinolines, the conditions for their synthesis are created only in the mesopores.

For the synthesis of basic *N*-heterocyclic compounds, pyridines and quinolines, we used amorphous mesoporous aluminosilicates (ASM), the preparation of which by the sol-gel method was described by us earlier [21, 22]. These mesoporous materials are characterized by a narrow distribution of mesopores with a size of 2–5 nm and are acidic.

The purpose of this work was to study the catalytic properties of samples of amorphous mesoporous aluminosilicate ASM with different Si/Al molar ratios (40, 80, 160) in the synthesis of pyridine and its alkyl derivatives in various ways: by reacting C<sub>2</sub>–C<sub>5</sub> alcohols with formaldehyde and ammonia, cyclic condensation of carbonyl compounds (acetic acid) aldehyde, propionic aldehyde) with ammonia, as well as a study of the activity and selectivity of the mesoporous aluminosilicate ASM in the synthesis of alkylquinolines, alkyltetrahydroquinolines and alkyl dihydroquinolines by the reaction of aniline with aldehydes and ketones.

## EXPERIMENTAL

### *Materials and Reagents*

For the synthesis of pyridines, alcohols (ethanol 96%, *n*-propanol 99%, *n*-butanol 99%, *n*-pentanol 99%, Acros), aqueous solutions of formaldehyde (37%, Acros) and ammonia (28%, analytical purity grade, Sigma Tech), acetaldehyde (99.5%, Acros), propionic aldehyde (99%, Acros) were used. Alkylquinolines, alkyltetrahydroquinolines, and alkyl dihydroquinolines were obtained from aniline (99.8%, Acros) and carbonyl compounds (Acros): propionic aldehyde (99%), butyric aldehyde (99%), and acetophenone (98%). The reagents were used without further purification.

### *Catalysts*

Mesoporous aluminosilicates were synthesized using the procedure developed by us based on the sol-gel method [21, 22]. The source of silicon was tetraethyl orthosilicate (TEOS) (98%, Acros Organics), the source of aluminum was Al(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O (99%, Merck), ethanol (98%) served as a solvent. Mesoporous

aluminosilicates ASM samples with Si/Al molar ratios of 40, 80, and 160, designated as ASM-40, ASM-80, and ASM-160, respectively, were obtained. The prepared aluminosilicate ASM samples were ground to powders, fraction <100 μm.

### *Physicochemical Study of the Catalysts*

The chemical composition of the obtained aluminosilicates was investigated by X-ray fluorescence spectrometry using an EDX-720/900hs instrument (Shimadzu, Japan).

The phase composition of the samples was analyzed on a D8 Advance diffractometer (Bruker, Germany) with monochromatic CuK<sub>α</sub> radiation in the range of 2θ angles from 5° to 40° with a step of 0.5°/min and a signal accumulation time at each point of 20 s.

The state of aluminum in the calcined samples was assessed by <sup>27</sup>Al NMR spectra. The spectra were recorded on an Avance-400 NMR spectrometer (Bruker, Germany) with a multi-core SD4 sensor in a simple single-pulse experiment with sample rotation at a magic angle (~10<sup>4</sup> Hz) in zirconia rotors. The external standard was an aqueous solution of AlCl<sub>3</sub> with a concentration of 1 mol/L.

The characteristics of the porous structure were determined using low-temperature adsorption-desorption of nitrogen (77 K) on an ASAP-2020 instrument (Micromeritics, USA). Before analysis, the samples were evacuated for 6 h at 350°C.

The acidic properties of aluminosilicates were studied by infrared (IR) spectroscopy using low-temperature adsorption of the CO probe molecule. Infrared spectra were recorded on an FTIR-8400 spectrometer (Shimadzu, Japan) in the range 700–6000 cm<sup>-1</sup>.

### *Synthesis of Pyridines and Quinolines*

**Synthesis of Pyridines** was carried out by interaction of alcohols (ethanol, *n*-propanol, *n*-butanol, *n*-pentanol) with formaldehyde and ammonia in a flow-type reactor with a fixed catalyst bed (1 g) at 300–400°C, atmospheric pressure, a space velocity (*w*) of 7 h<sup>-1</sup>, and a molar ROH : CH<sub>2</sub>O : NH<sub>3</sub> ratio of 1.0 : 0.8 : 1.5. After the reaction, the reactor was purged with nitrogen. The reaction products collected in an ice-cooled trap were extracted with diethyl ether and analyzed by gas-liquid chromatography (GLC).

**5-Ethyl-2-methylpyridine** was obtained by the reaction of acetaldehyde with ammonia in an autoclave at 150°C and a molar CH<sub>3</sub>COH : NH<sub>3</sub> ratio of 1 : 3. The catalyst concentration was 10 wt %. The reaction time was 5 h. The reaction products were extracted with methylene chloride and analyzed using GLC. The reaction mass was filtered from the catalyst and isolated by chromatography using a 200-mm column

with 30 g SiO<sub>2</sub> (eluent, a mixture of hexane and ethyl acetate (20 : 80)).

**2-Ethyl-3,5-dimethylpyridine** was obtained by the reaction of propionic aldehyde with ammonia in a flow-type reactor at 300°C, atmospheric pressure,  $w = 5.2 \text{ h}^{-1}$ , and propionic aldehyde : NH<sub>3</sub> molar ratio of 1 : 3. The reaction products were extracted with diethyl ether and analyzed by the GLC method.

GLC analysis of pyridines was carried out on a Vega Series 2 GC-6000 chromatograph (Carlo Erba Strumentazione, Italy) with a flame ionization detector (packed column, 3 m, phase 15% PEG-6000 on Khromaton); the temperature of analysis was 50–200°C with programmed heating at a rate of 8°C/min; the temperature of the detector was 200°C; the temperature of the evaporator was 200°C; the carrier gas was helium (30 mL/min).

**Dialkylquinolines and dialkyltetrahydroquinolines** were synthesized by the reaction of aniline with aldehydes (C<sub>3</sub>, C<sub>4</sub>) in an autoclave at 160°C and atmospheric pressure; 6 h; the catalyst content was 20 wt %, the aniline : aldehyde molar ratio was 1 : 2. After the reaction cessation, the autoclave was cooled to room temperature and the ampoule was opened. The reaction mass was filtered from the catalyst and isolated by chromatography on a SiO<sub>2</sub> column (eluent, hexane → hexane–ethyl acetate mixture).

**Alkyldihydroquinoline** was obtained by the reaction of aniline with acetophenone in an autoclave at 130°C and an atmospheric pressure of 5 h; the catalyst content was 30 wt %; the aniline: acetophenone molar ratio was 1 : 2. After the reaction cessation, the autoclave was cooled to room temperature and the ampoule was opened. The reaction mass was filtered from the catalyst and isolated by chromatography on a SiO<sub>2</sub> column (eluent, hexane → hexane–ethyl acetate mixture).

The reaction products (dialkylquinolines, dialkyltetrahydroquinolines, alkyl dihydroquinolines) were analyzed using GLC on a GC-9A chromatograph (Shimadzu, Japan) with flame ionization detector, packed column (3 m), phase SE-30, programmed heating 50–250°C, and helium carrier gas.

Mass spectra were obtained on a GCMS-QP2010Plus chromatograph/mass spectrometer (Shimadzu, Japan) with a SPB-5 phase, capillary column 30 m × 0.25 mm, helium carrier gas, programmed

temperature 40–300°C, an ion source temperature of 200°C, and an ionization energy of 70 eV).

<sup>1</sup>H and <sup>13</sup>C NMR and homo- and heteronuclear COSY, HSQC, HMBC spectra were recorded using an Avance-400 instrument (Bruker, Germany; the working frequency for <sup>1</sup>H was 400.13 MHz and that for <sup>13</sup>C, 100.62 MHz) and an Avance III 500 HD Ascend instrument (Bruker, Germany; the working frequency for <sup>1</sup>H was 500.17 MHz; for <sup>13</sup>C, 125.78 MHz), CDCl<sub>3</sub> solvent.

## RESULTS AND DISCUSSION

### *Physicochemical Properties of Catalysts*

The physicochemical properties of the mesoporous aluminosilicate were studied in detail in [21, 22]. Information on the characteristics of the porous structure and acidic properties are presented in Table 1.

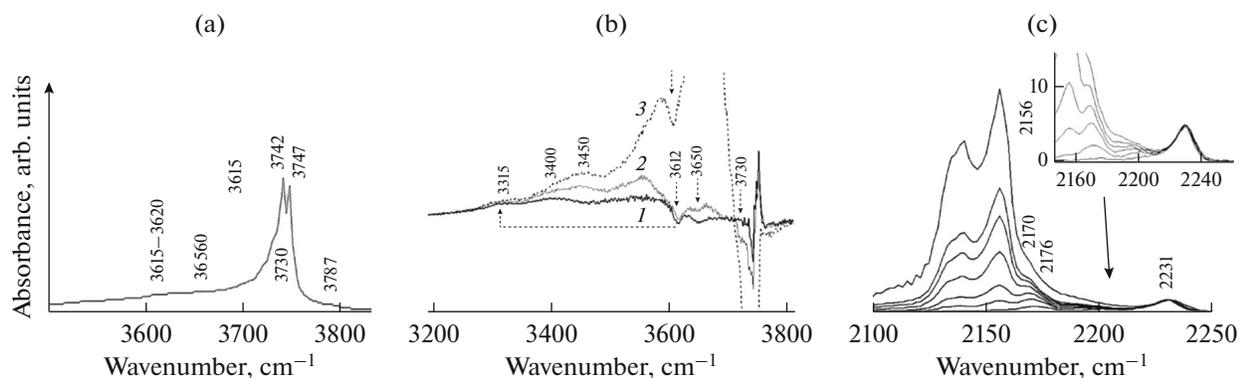
ASM samples were characterized by a narrow size distribution of mesopores from 2 to 5 nm; the mesopore volume was in the range 0.50–0.80 cm<sup>3</sup>/g; the BET specific surface area was 520–670 m<sup>2</sup>/g.

Brønsted (BAS) and Lewis (LAS) groups were found on the surface of the ASM samples. Figure 1 shows the IR spectra of the ASM-80 sample in the region of stretching vibrations of OH groups before and after CO adsorption. In the IR spectrum (Figs. 1a, 1b) absorption bands of hydroxyl groups of several types are observed: strong BAS of type I (the value of shift is  $\Delta\nu_{\text{OH}} = 300 \text{ cm}^{-1}$ ), which refer to bridging Si–O(H)–Al groups, and strong BAS of type II (the value of shift is  $\Delta\nu_{\text{OH}} = 270\text{--}320 \text{ cm}^{-1}$ ), which belong to the Si–O(H)...Al<sup>3+</sup> or Al–O(H)–Al groups. On the sample surface, there are also weak acidic silanol groups (absorption bands at 3742 and 3747 cm<sup>-1</sup> in the IR spectrum before CO adsorption; the value of shift is  $\Delta\nu_{\text{OH}} = 90\text{--}150 \text{ cm}^{-1}$ ).

According to IR spectroscopic data of adsorbed CO on the sample surface, there are three types of Lewis acid sites. In the IR spectrum (Fig. 1c), there are absorption bands at 2223 and 2231 cm<sup>-1</sup>, which are characteristic of CO complexes with Al<sup>3+</sup> ions in the pentahedral coordination and are typical structural defects of aluminosilicates and zeolites, absorption bands at 2210–2212 cm<sup>-1</sup>, which refer to medium-strength LASs, and absorption bands at 2202–2200

**Table 1.** Physicochemical characteristics of mesoporous aluminosilicates

Sample	Si/Al	Pore volume, cm <sup>3</sup> /g		Specific surface area $S_{\text{BET}}$ , m <sup>2</sup> /g	Average pore size $D$ , nm	Concentration of acid centers, μmol/g	
		$V_{\text{micro}}$	$V_{\text{meso}}$			LAS	BAS
ASM-40	40	0.05	0.50	670	4	162	50
ASM-80	80	0.05	0.71	640	4	119	27
ASM-160	120	0.05	0.80	520	4	74	15



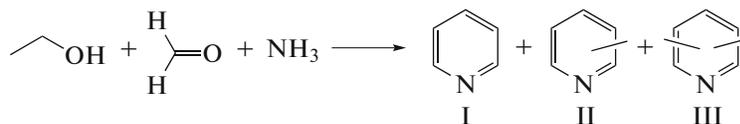
**Fig. 1.** (a) IR spectrum of the ASM-80 sample in the region of oscillations of surface hydroxyl groups; (b) IR difference spectra in the region of stretching vibrations of surface hydroxyl groups for the ASM-80 sample at a CO pressure of (1) 0.2, (2) 0.3, and (3) 5 (3) Torr; (c) IR spectra of CO adsorbed on the ASM-80 sample in the region of stretching vibrations of carbonyl groups with an increase in CO pressure in a range from 0.1 to 10 Torr.

and  $2190\text{ cm}^{-1}$ , which refer to the CO complex with  $\text{Al}^{3+}$  ions, and apparently alumina clusters. Types of acid sites are close to those observed for amorphous aluminosilicates. [23]. The ASM-40 sample has the maximum concentration of both BASs and LASs. On the ASM-80 and ASM-160 samples, the concentration of acid sites is lower (Table 1).

#### Catalytic Properties of Mesoporous Aluminosilicate ASM in the Synthesis of *N*-Heterocyclic Compounds

**Synthesis of pyridines by the reaction of alcohols  $\text{C}_2\text{--C}_4$  with formaldehyde and ammonia.** The synthesis

of pyridine and its methyl derivatives was carried out by the reaction of ethanol with formaldehyde and ammonia, which was first carried out under the action of ZSM-5 zeolites [24]. Both on zeolite catalysts and on amorphous mesoporous aluminosilicate ASM samples, the main products of this reaction are pyridine (I), picolines (2-, 3-, and 4-methylpyridines) (II), and lutidines (dimethylpyridines) (III) (Scheme 1). In the composition of picolines, 3-methylpyridine accounts for 80%. In the composition of lutidines, 3,5-isomer prevails. Also, compounds that are heavier than dimethylpyridines are formed.



**Scheme 1.**

The results of the study of the catalytic properties of mesoporous aluminosilicates ASM (with molar ratios of  $\text{Si}/\text{Al} = 40, 80, \text{ and } 160$ ), differing in acid characteristics in the reaction of ethanol, formaldehyde, and ammonia, are given in Table 2.

It was found that the ASM-40 sample is the most active in the reaction. The conversion of ethanol on mesoporous aluminosilicate samples decreases in the series  $\text{ASM-40} > \text{ASM-80} > \text{ASM-160}$ , which is associated with a decrease in the concentration of acid sites due to a decrease in the fraction of aluminum atoms in the aluminosilicate framework. The data obtained show that the catalytic systems ASM are active in the studied reaction only if they contain a certain number of strong acid sites. A decrease in the BAS concentration below a certain level leads to the loss of catalyst activity, which cannot be compensated by the accessibility of sites.

In the reaction products formed under the action of the studied catalysts, picolines (mainly 3-methylpyridine) have the highest content: 49–57%. Picolines are formed most selectively on the samples of mesoporous aluminosilicates with  $\text{Si}/\text{Al}$  molar ratios of 40 and 80. An increase in the ratio of framework atoms of  $\text{Si}/\text{Al}$  aluminosilicate samples from 40 to 160 leads to an increase in the selectivity to pyridine and lutidines, and the selectivity to picolines and heavy compounds decreases.

We compared the activity and selectivity of mesoporous aluminosilicates ASM with the properties of microporous catalysts: H-ZSM-5 and Pb-ZSM-5 zeolites [24]. It can be seen from the data presented in Table 2 that the conversion of ethanol at similar temperatures (400 and  $420^\circ\text{C}$ ) on ASM-40 sample is slightly higher than on the most active zeolite H-ZSM-5. Taking into account that experiments on the

**Table 2.** Synthesis of pyridines on mesoporous aluminosilicates ASM by the reaction of ethanol, formaldehyde, and ammonia\*

Catalyst	$T, ^\circ\text{C}$	Alcohol conversion, %	Selectivity, %				Reference
			pyridine (I)	picolines (II)	lutidines (III)	heavy products	
ASM-40	300	50	19	57	18	6	This work
ASM-80	300	30	20	56	22	2	This work
ASM-160	300	10	24	49	25	2	This work
ASM-40	400	80	18	47	24	11	This work
H-ZSM-5** (Si/Al = 150)	420	72.5	53	32	15	Not determined	24
Pb-ZSM-5**	400	44.9	53	32	15	Not determined	24

\* Reaction conditions: molar ratio  $\text{C}_2\text{H}_5\text{OH} : \text{CH}_2\text{O} : \text{NH}_3 = 1.0 : 0.8 : 1.5$ ,  $w = 7 \text{ h}^{-1}$ . \*\* $w = 0.5 \text{ h}^{-1}$ .

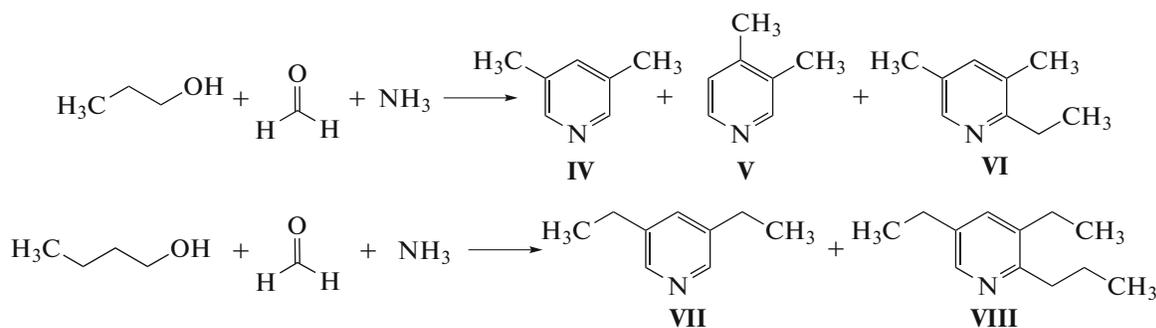
ASM-40 samples were carried out at a higher feed space velocity of ( $7 \text{ h}^{-1}$ ) than on H-ZSM-5 and Pb-ZSM-5 zeolites ( $0.5 \text{ h}^{-1}$ ) and that alcohol conversion increases with a decrease in  $w$ , we can speak quite confidently about the high activity of mesoporous aluminosilicates ASM in the synthesis of pyridines by the reaction of ethanol, formaldehyde, and ammonia.

When comparing the composition of products formed on zeolite catalysts and amorphous aluminosilicates, it is clear that the reaction mass obtained on mesoporous aluminosilicate is rich in methylpyridines: picolines and lutidines. The pyridine : picolines : lutidines ratio in the products synthesized in the pres-

ence of H-ZSM-5 and Pb-ZSM-5 zeolites is 1 : 0.6 : 0.3, while for the ASM-40 sample, this ratio is 1 : 3 : 1.

The presented data convincingly show the applicability of amorphous mesoporous aluminosilicates with acidic properties in the synthesis of pyridines by the reaction of ethanol, formaldehyde and ammonia. The activity of ASM-40 mesoporous aluminosilicate sample is not inferior to the H-ZSM-5 and Pb-ZSM-5 zeolite catalysts, and the total selectivity of the formation of picolines and lutidines on it reaches 75–78%.

The reaction of other alcohols (*n*-propanol and *n*-butanol) with formaldehyde and ammonia occurs in the presence of mesoporous aluminosilicates ASM to form mainly 3,5-dialkylpyridines (Scheme 2).



In the case of *n*-propanol, 3,5-lutidine (IV) is the main product of the reaction. In the case of *n*-butanol, 3,5-diethylpyridine (VII) is the main product. In addition to dialkylpyridines (IV) and (VII), light compounds are also present in the reaction products, among which both linear condensation products of alcohol, formaldehyde, and ammonia (imines, propyl, and butylamines, acetal) and 3-methylpyridine are identified. In the reaction with *n*-propanol, 3,4-lutidine (V) and a mixture of trialkylpyridines with a predominant content of 2-ethyl-3,5-dimethylpyridine (VI) are formed along with 3,5-lutidine (IV). In the

reaction with *n*-butanol, the main by-product is 2-propyl-3,5-diethylpyridine (VIII). Data presented in Table 3 show that the ASM-40 sample has a high selectivity in the synthesis of 3,5-dialkylpyridines. In the reaction of *n*-propanol with formaldehyde and ammonia at  $300^\circ\text{C}$ , the selectivity to 3,5-lutidine is 97% with an alcohol conversion of 25%. As the temperature increases to  $400^\circ\text{C}$ , alcohol conversion increases to 70%, but the amount of by-products in the reaction mass increases, as a result of which the selectivity to dialkylpyridine decreases. Similar dependences were observed in the interaction of *n*-butanol

**Table 3.** Synthesis of 3,5-dialkylpyridines on ASM-40 mesoporous aluminosilicate and zeolite catalysts\*

Catalyst	Alcohol	<i>T</i> , °C	Alcohol conversion, %	Selectivity, %				Reference
				light products	3,5-di-alkylpyridines	other di- and trialkylpyridines	heavy products	
ASM-40	<i>n</i> -propanol	300	25	3	97	—	—	this work
ASM-40	<i>n</i> -propanol	350	45	5	84	11	—	this work
ASM-40	<i>n</i> -propanol	400	70	6	79	15	—	this work
ASM-40	<i>n</i> -butanol	300	22	3	86	11	—	this work
ASM-40	<i>n</i> -butanol	400	62	11	63	26	—	this work
ASM-40	<i>n</i> -pentanol	400	20	25	40	25	10	this work
HY	<i>n</i> -propanol	400	16	11	63	23	3	this work
HY	<i>n</i> -butanol	400	14	30	41	28	1	this work
La-ZSM-5**	<i>n</i> -propanol	400	88.6	25.1	72.2	2.7	not determined	25
H-ZSM-5***	<i>n</i> -butanol	400	91.2	12	69	19	not determined	26

Dashes mean that the corresponding products are not formed. \* Reaction conditions: molar ratio ROH : CH<sub>2</sub>O : NH<sub>3</sub> = 1.0 : 0.8 : 3.0; 400°C, *w* = 7 h<sup>-1</sup>. \*\* C<sub>3</sub>H<sub>7</sub>OH : CH<sub>2</sub>O : CH<sub>3</sub>OH : NH<sub>3</sub> = 1.0 : 0.4 : 0.9 : 6, 400°C, *w* = 0.5 h<sup>-1</sup>. \*\*\* C<sub>4</sub>H<sub>9</sub>OH : CH<sub>2</sub>O : NH<sub>3</sub> = 1 : 1 : 6, 400°C, *w* = 0.5 h<sup>-1</sup>.

with formaldehyde and ammonia: with increasing temperature from 300 to 400°C, the conversion of alcohol increases from 22 to 62%, and the selectivity to 3,5-diethylpyridine drops from 86 to 63%.

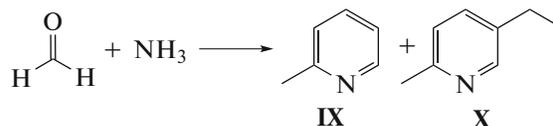
Further elongation of the hydrocarbon chain of the alcohol (*n*-pentanol) worsens the reaction performance: even at 400°C, the conversion of alcohol does not exceed 20%, and a complex mixture of products is formed, in which the content of 3,5-dipropylpyridine is 40%.

Comparison of the catalytic properties of the ASM-40 sample and microporous HY zeolite with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 5.0 (our data) in the interaction of *n*-propanol/*n*-butanol with formaldehyde and ammonia showed that the selectivity to dialkylpyridines and the alcohol conversion are higher on the ASM-40 sample (Table 3). The appearance of a large number of by-products on the HY zeolite can be associated with a significant concentration of nonuniform active sites in it, including strong Brønsted acid sites.

When comparing the results obtained in this work with the literature data, it can be seen (Table 3) that mesoporous aluminosilicate ASM is close to the La-ZSM-5 zeolite (the reaction of *n*-propanol with formaldehyde, methanol, and ammonia [25]) and the H-ZSM-5 zeolite (the interaction of *n*-butanol with formaldehyde and ammonia [26]) on the selectivity to dialkylpyridines (IV) and (VII), but its activity is lower.

The reactions of aldehydes with ammonia lead to the formation of di- and trialkylpyridines. One of the

most important industrial reactions is the interaction of acetaldehyde with ammonia to form 2-methyl-5-ethylpyridine (X), which is the main raw material in the production of nicotinic acid and 2-methyl-5-vinylpyridine (Scheme 3).

**Scheme 3.**

It is known that in industry, methyl ethyl pyridine (X) is produced by the reaction of paraldehyde (acetaldehyde trimer) with ammonia in the liquid phase at 200–250°C and 5–10 MPa in the presence of ammonium salts (e.g., ammonium acetate) or acetic acid. The yield of methyl ethyl pyridine in this reaction reaches 60% [19].

The reaction of acetaldehyde with ammonia on the ASM-40 sample occurs with the formation of predominantly methyl ethyl pyridine (X), the selectivity to which under these conditions is 88% with an acetaldehyde conversion of 60%. 2-Methylpyridine (IX) is found in a small amount. On the microporous HY zeolite, with which we compared the ASM-40 sample, the conversion of acetaldehyde is higher: 69%. This is due to the higher acidity of the HY catalyst (Table 4). Apparently, for the same reasons the selectivity of HY zeolite is 1.8 times lower than that on the ASM-40 sample and a significant amount of heavy compounds

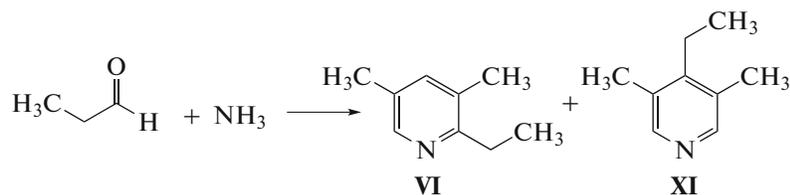
**Table 4.** The interaction of acetaldehyde with ammonia on ASM-40 aluminosilicate

Catalyst	Acetaldehyde conversion, %	Selectivity, %		
		2-methylpyridine (IX)	methylethylpyridine (X)	heavy products
ASM-40	60	3	88	9
HY	69	5	55	40

Reaction conditions: acetaldehyde : NH<sub>3</sub> = 1 : 3, 150°C, 10% of catalyst.

appear, which are different di- and trialkylpyridines. A comparison of our results with literature data shows that the yield of methyl ethyl pyridine (X) (53%) is close to that observed in industrial units.

The reaction of propionic aldehyde with ammonia leads to the formation of a mixture of mono-, di- and trialkylpyridines, among which 2-ethyl-3,5-dimethylpyridine (VI) (Scheme 4) is the main product.

**Scheme 4.**

In addition to 2-ethyl-3,5-dimethylpyridine (VI), the following products were identified: imines (designated as light products), pyridine (I), 3- and 4-methylpyridines, dimethylpyridines, 3,5-dimethyl-4-ethylpyridine, and compounds heavier than 4-ethyl-3,5-dimethylpyridine (XI). The conversion of propionic aldehyde and the composition of products formed on various samples of zeolite catalysts are given in Table 5.

Under conditions studied (150–300°C, 7 h<sup>-1</sup>), the conversion of propionic aldehyde on the ASM-40 sample reaches 70–91%, the selectivity to 2-ethyl-3,5-dimethylpyridine (VI) is 40–41%, and the amount of heavy compounds does not exceed 10%. The highest selectivity to 2- and 4-ethyl-3,5-dimethylpyridines (VI) and (XI) was observed at 300°C (their overall selectivity was 57%).

On microporous HY zeolite at 300°C, aldehyde conversion is lower (85%) and the reaction occurs with the formation of a larger amount of heavy com-

pounds, which is apparently associated with the increased acidity of HY zeolite.

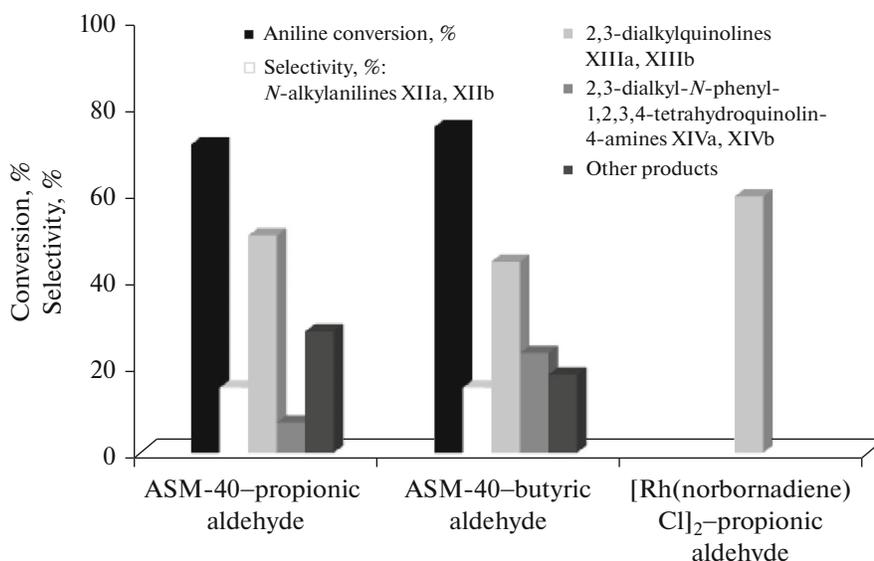
It was of interests to compare the results obtained with those already known. It turned out that the reaction of propionic aldehyde with ammonia under the action of Pb-ZSM-5 zeolite mentioned in [27] takes place at 400°C and 0.5 h<sup>-1</sup> with an aldehyde conversion of 69.5%. The authors of [27] describe the product composition as a mixture of 2,6-lutidine (10%), 3,5-lutidine (15%), pyridine, and collidines (75%). Information on the selective formation of 2-ethyl-3,5-dimethylpyridine (VI) is missing.

**Synthesis of quinolines and dihydroquinolines.** Synthesis of quinolines and dihydroquinolines. Most often, for the synthesis of quinolines, the Skraup, Döbner–Von Miller, Friedländer, and Combes methods are used with acid or base catalysts. Most of the proposed methods are characterized by several stages, severe reaction conditions, and low yields of the target products.

**Table 5.** Synthesis of 2-ethyl-3,5-dimethylpyridine (VI) in the presence of zeolite catalysts

Catalyst	T, °C	Propionic aldehyde conversion, %	Selectivity to product, %					
			light products	pyridine (I), picolines	2,6-lutidine	2-ethyl-3,5-dimethylpyridine (VI)	4-ethyl-3,5-dimethylpyridine (XI)	heavy products
HY	300	85	26	8	—	43	8	15
ASM-40	150	70	23	15	10	40	9	3
ASM-40	300	91	24	4	5	41	16	10

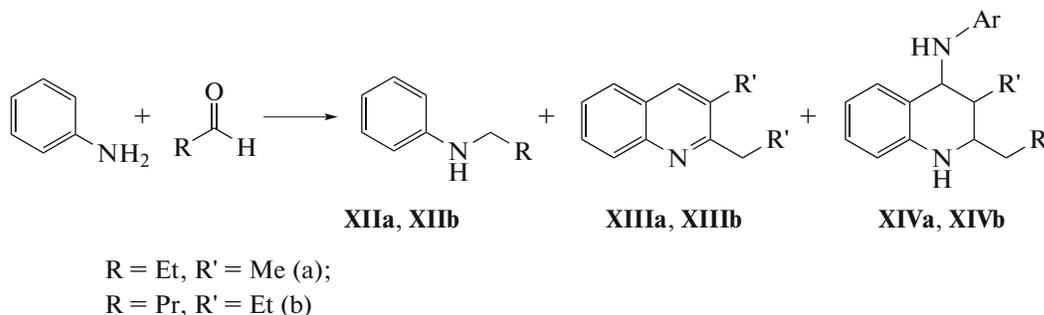
Reaction conditions: molar ratio propionic aldehyde : ammonia = 1 : 3, w = 7 h<sup>-1</sup>. A dash means that the corresponding product is not formed.



**Fig. 2.** The interaction of aniline with aldehydes C<sub>3</sub>, C<sub>4</sub> in the presence of mesoporous aluminosilicate ASM-40 sample. The aniline : aldehyde molar ratio is 1 : 2; 160°C; 20% catalyst; the solvent is chlorobenzene.

We attempted to synthesize dialkylquinolines in the presence of the ASM-40 sample by the reaction of aniline with aldehydes (propionic and butyric). It was found that the products of this reaction are *N*-alkylanilines (**XIIa**, **XIIf**), 2,3-dialkylquinolines (**XIIIa**, **XIIIb**), and 2,3-dialkyl-*N*-phenyl-1,2,3,4-

tetrahydroquinolin-4-amines (**XIVa**, **XIVb**) (Scheme 5). In addition to compounds (**XII**)–(**XIV**), aldehyde condensation products, dialkyl dihydroquinolines, and heavy compounds are present in the reaction mass. They are indicated in Fig. 2, like “others.”



**Scheme 5.**

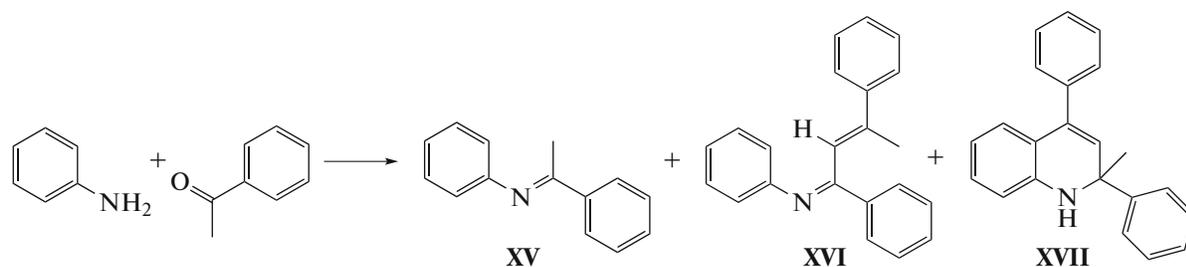
Under the conditions studied, the conversion of aniline upon interaction with propionic and butyric aldehydes is rather high: 71 and 75%, respectively (Fig. 2). In the composition of the reaction products with propionic aldehyde, the main compound is dialkylquinoline (**XIIIa**), the selectivity to which reaches 50%. Two main products, dialkylquinoline (**XIIIb**) and tetrahydroquinoline (**XIVb**), were found in a ratio of about 2 : 1 in the reaction of aniline with butyric aldehyde. The selectivity to *N*-alkylanilines (**XIIa**, **XIIf**) in both reactions was 15%.

A comparison of the yield of dialkylquinoline (**XIIIa**) obtained in the presence of the ASM-40 sample (39%) and [Rh(norbornadiene)Cl]<sub>2</sub> (59%) [28]

showed that Rh catalytic systems are more effective in the reaction of aniline with propionic aldehyde.

One of the simplest and most convenient methods for producing dihydroquinolines is acid-catalyzed interaction of aniline with ketones [29, 30]. Earlier [31], we demonstrated that the ASM-40 sample allows the synthesis of 2,2,4-trimethyl-1,2-dihydroquinoline from aniline and acetone.

The reaction of aniline with acetophenone on amorphous aluminosilicates occurs with the formation of three main products: (*E*)-*N*-(1-phenylethylidene)aniline (**XV**), (1*E*,2*E*)-*N*-(1,3-diphenylbut-2-en-1-ylidene) aniline (**XVI**) and 2-methyl-2,4-diphenyl-1,2-dihydroquinoline (**XVII**) (Scheme 6).



Scheme 6.

Also, acetophenone aldol condensation can occur with the formation of 2(Z,E)-1,3-diphenylbut-2-ene-1-one and the trimerization of acetophenone in the presence of aniline with the formation of 1,3,5-triarylbenzene, indicated in Table 6 as “others.”

In the reaction of aniline with acetophenone, the ASM-40 sample is less active than in the reaction with acetone, as evidenced by a lower conversion of aniline (57 and 85%, respectively). The selectivity to dihydroquinoline (XVII) is 45%. The imines (XV) and (XVI) formed are the products of the interaction of aniline with both the initial acetophenone and acetophenone dimer, which are formed in parallel in the reaction mass under the conditions studied.

It should be noted that, on microporous aluminosilicates (zeolite HY), the formation of imine (XVI), as well as dihydroquinoline (XVII) does not occur. The only product in this case is the Schiff base (XV), which is formed as a result of the condensation of aniline with acetophenone.

The results obtained indicate a significant dependence of the activity and selectivity of the studied catalysts on their textural characteristics. Since most of the active centers in zeolites (strongly acidic structural OH groups) are known to be located inside channels or cavities, their accessibility to reacting molecules is the main factor determining catalytic properties. The low activity of zeolite HY and the predominant formation of linear condensation product (XV) on it, rather than the bulk dihydroquinoline molecule (XVII), are due to the molecular sieve effect of the microporous zeolite crystal lattice. Furthermore, the reason for the low activity of zeolite HY can be not only spatial hin-

drances for the diffusion and interaction of reagents, but also the blocking large cavities with dihydroquinoline molecules (XVII) formed, which is due to the fact that the diameter of the entrance windows to the large cavity is smaller than the diameter of the cavity (0.75 and 1.2 nm, respectively) [32].

In the mesopores of the ASM-40 sample, steric hindrances to the formation of more bulky molecules than imine (XV) are absent. Therefore, not only linear condensation of aniline with acetophenone, but also other reactions take place: condensation of aniline with acetophenone dimer and the subsequent heterocyclization of compound (XVI) leading to the formation of dihydroquinoline (XVII).

## CONCLUSIONS

As a result of studying the catalytic properties of amorphous mesoporous aluminosilicates ASM with different Si/Al molar ratios (40, 80, and 160) in the synthesis of basic N-heterocyclic compounds (pyridines and quinolines) it was found that the ASM-40 sample (Si/Al = 40) it is most effective in the studied cyclocondensation reactions of alcohols/carbonyl compounds with ammonia/amines. This sample has the maximum concentration of acid sites.

The interaction of ethanol with formaldehyde and ammonia in the presence of aluminosilicate ASM-40 sample takes place with an alcohol conversion of 50–80% at 300–400°C. The reaction mass obtained on samples of mesoporous aluminosilicates is characterized by a high content of methylpyridines (up to 57%

**Table 6.** The interaction of aniline with acetophenone in the presence of mesoporous ASM-40 aluminosilicate

Catalyst	Ketone	Aniline conversion, %	Selectivity to product, %			
			(E)-N-(1-phenylethylidene)aniline (XV)	(1E,2E)-N-(1,3-diphenylbut-2-en-1-ylidene)aniline (XVI)	2-methyl-2,4-diphenyl-1,2-dihydroquinoline (XVII)	others
ASM-40	Acetophenone	57	18	23	45	14
HY	Acetophenone	79	100	0	0	–

Reaction conditions: molar ratio aniline : acetophenone = 1 : 2; 30% of the catalyst; 130°C;  $w = 5 \text{ h}^{-1}$ . A dash means that the corresponding products are not formed.

picolin and 24% lutidines) and a low content of heavy compounds.

The main product of the reaction of *n*-propanol with formaldehyde and ammonia on the ASM-40 sample is 3,5-lutidine, which is formed with a selectivity of up to 97% at a conversion of 25% (300°C). The interaction of *n*-butanol with formaldehyde and ammonia on HY zeolite led to the synthesis of 3,5-diethylpyridine with a selectivity of 86% at a conversion of 22% (300°C).

The aluminosilicate ASM-40 sample enables the formation of 5-ethyl-2-methylpyridine in the reaction of acetaldehyde with ammonia with a selectivity of 88% with an aldehyde conversion of 60%. The interaction of propionic aldehyde with ammonia on the aluminosilicate ASM-40 sample occurs with the formation of 2- and 4-ethyl-3,5-dimethylpyridines, the overall selectivity to which is 57% at an aldehyde conversion of 91%.

Aniline reacts with aldehydes (C<sub>3</sub>, C<sub>4</sub>) with the formation of 2,3-dialkylquinolines and 2,3-dialkyltetrahydroquinolines with an overall selectivity of 57–67%.

It is shown that aniline and acetophenone in the presence of mesoporous aluminosilicate ASM-40 sample under the studied conditions give a mixture of (E)-*N*-(1-phenylethylidene)aniline, (1E,2E)-*N*-(1,3-diphenylbut-2-en-1-ylidene)aniline and 2-methyl-2,4-diphenyl-1,2-dihydroquinoline, in which 2-methyl-2,4-diphenyl-1,2-dihydroquinoline prevails (45%).

The high activity and selectivity of the mesoporous aluminosilicate ASM in the synthesis of bulk molecules of alkylpyridines and alkylquinolines compared to microporous zeolites is achieved due to the presence of meso- and macropores in its structure, which increase the accessibility of acid sites. Such a mesoporous structure makes it possible to reduce the diffusion hindrances for the movement of reactant molecules and reaction products, and to reduce pore blocking. In addition, in the mesopores, the concentration of reacting molecules may be higher, which leads to an increase in the number of chemical interaction acts of the reactants and an increase in their conversion. Another factor favoring the selective formation of target products may be the presence of a small amount of acid sites of aluminosilicate ASM with a lower strength than in zeolite catalysts, which prevents the occurrence of side reactions with the formation of significant amounts of heavy compounds and coke leading to catalyst deactivation.

#### FUNDING

The work was carried out as part of the state assignment AAAA-A17-117012610058-4 and with the financial support from the Russian Science Foundation (Russian–Indian grant no. 16-43-02010).

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*Translated by Andrey Zeigarnik*