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Synthesis of *N*-Methylaniline over Molecular Sieve Catalysts

M. V. Belova[a], O. A. Ponomareva[a, b], and I. I. Ivanova[a, b]
[a] *Moscow State University, Moscow, Russia*
[b] *Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia*
e-mail: belova.msu@gmail.com

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Abstract—The preparation of *N*-methylaniline in two various processes: alkylation of aniline with methanol and hydroalkylation of nitrobenzene with methanol has been studied. Bifunctional molecular sieves containing metal copper as the hydrogenating component and zeolites BEA, MOR, MFI, FAU (Y) and mesoporous material MCM-41 as an alkylating component were used as catalysts. It has been shown that the modification of samples with copper nitrate increases the number of Lewis acid sites and decreases the number of Brønsted acid sites as copper embeds into cation exchange positions. It has been determined that the catalyst modification with copper increases the activity and enhances the selectivity towards *N*-alkylated products.

Keywords: aniline, nitrobenzene, methanol, *N*-methylaniline, alkylation, hydroalkylation, zeolites, molecular sieves

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Zeolites and mesoporous molecular sieves are promising heterogeneous catalysts that combine high environmental friendliness, unique porous structure and ability to be modified to give catalysts with acidic, basic or redox properties. On the basis of zeolites, the multifunctional systems capable of catalyzing multistep reactions may be synthesized by introducing metals using ion exchange or impregnation techniques [1]. As a result of numerous advantages over homogeneous catalysts, molecular sieve catalysts are widely used in various petrochemical and petroleum refining processes. In particular, high activity parameters are achieved in the processes of alkylation of aromatic compounds, such as benzene alkylation with the formation of ethylbenzene and cumene [2, 3], alkylation of phenol with various alcohols and alkenes [4–6], and aniline alkylation with methanol [7, 8].

The alkylation of aniline with methanol is an industrially important reaction due to a wide range of applications of substituted anilines: *N*-methylaniline (NMA), *N,N*-dimethylaniline (NNDMA), and toluidines (T). *N*-alkylated products are valuable raw materials for the synthesis of organic compounds and are used as additives in the production of dyes, synthetic rubbers, herbicides, and explosives [8, 9]. The reaction of aniline methylation has been studied over oxide catalysts [10]; spinels $Cr_xMn_yFe_2O_4$ [11] and $CuCr_{2-x}Fe_xO_4$ [12]; aluminophosphates $AlPO_4$ [13]; zeolites of various structural types such as MFI [8, 14, 15], Y [14, 15], and BEA [16]; and mesoporous materials MCM-41 [9] and SBA-15 [17].

Moreover, it has been shown that *N*-methylaniline can be obtained not only via direct alkylation of aniline, but also in one step via hydroalkylation of nitrobenzene with methanol [18] since both processes can be carried out on similar catalytic systems and under close conditions. The catalyst for the one-step *N*-methylaniline synthesis should be bifunctional and combine both hydrogenating and alkylating functions. Metals are used as a hydrogenating component and molecular sieves can be used as an alkylating component. Metallic copper supported on SiO_2 is known to be an industrial catalyst for nitrobenzene hydrogenation [19]; besides, copper-containing catalysts based on various metal oxides exhibit high activity in aniline alkylation with methanol [10]. Therefore it can be assumed that the modification of molecular sieves with copper could increase their activity in both aniline alkylation and nitrobenzene hydroalkylation with methanol. In this paper, these two processes were investigated in the presence of copper-modified molecular sieves. For comparative analysis were examined the catalytic activity of the H-forms of these molecular sieves and the influence of their acidic characteristics and modification with copper on their physicochemical and catalytic properties.

EXPERIMENTAL

The commercially available zeolites MFI (SiO_2/Al_2O_3 = 80), BEA (SiO_2/Al_2O_3 = 75), MOR (SiO_2/Al_2O_3 = 97), and FAU(Y) (SiO_2/Al_2O_3 = 60) (Zeolyst) were used as the zeolite component of the catalyst. The mesoporous material MCM-41 with the ratio of $SiO_2/Al_2O_3 = 50$ was synthesized according to a published procedure [20] and then subjected to the triple ion exchange with ammonium nitrate solution. In order to obtain the H-forms of zeolites and MCM-41, the NH_4-forms of the samples were calcined in a flow of dry air at 550°C for 6 h. The modification of the catalysts with copper was conducted using incipient wetness impregnation of the parent zeolite with an aqueous copper nitrate solution taken in amount to obtain 7.5 wt % metal loading. The prepared samples were dried at 100°C, calcined in a flow of dry air at 400°C for 6 h, and reduced *in situ* prior to the experiment at 300°C in a hydrogen stream for 30 min.

Low-temperature nitrogen adsorption/desorption isotherms were measured using a Micromeritics ASAP2000 automated porosimeter. All the samples were preliminarily evacuated at 350°C to 10^{-3} Pa. The total adsorption pore volume was calculated from the amount of nitrogen adsorbed at a relative pressure $p/p_0 = 0.945$. The surface area was calculated using a Brunauer–Emmett–Teller (BET) method. The micropore volume was determined using the de Boer–Lippens *t*-plot method. The mesopore volume was determined by the Barrett–Joyner–Halenda (BJH) method in pores with a size of 10–100 Å.

The acidic properties of the samples were studied using temperature-programmed desorption of ammonia (TPD NH_3) on a sorption analyzer USGA-101 (Unisit). The sample was calcined in a flow of dry helium at 550°C and then cooled to room temperature. The adsorption of ammonia was conducted for 30 min at 60°C, ammonia was diluted with nitrogen in a 1 : 1 ratio. Physically sorbed ammonia was removed in a flow of dry helium at 100°C for 1 h. The experiments on the TPD NH_3 were conducted in the temperature range of 60–800°C in a flow of dry helium (flow rate of 30 mL/min). The heating rate was 8°C/min.

IR spectra were recorded on a Nicolet Protege 380 Fourier transform spectrometer. The spectrometer was equipped with an MCT detector, the recording in the region of structural vibrations was conducted within the range of 1700–400 cm^{-1} with the resolution of 4 cm^{-1}. The adsorption of pyridine (Py) was carried out on a vacuum unit that operated at a vacuum of 5×10^{-4} Pa and was equipped with absolute pressure sensors. Before the experiment catalyst samples were evacuated, heated to 450°C at a rate of 0.5°C/min, and calcined at that temperature until a vacuum of $\leq 1 \times 10^{-3}$ Pa was reached. The adsorption of pyridine was performed at 150°C and a Py pressure of 3 Torr followed by the evacuation at 150°C for 1 h. The obtained IR spectra were processed using the OMNIC ESP 7.3 software package.

The redox properties of the catalysts were studied using temperature-programmed reduction by hydrogen (TPR H_2) on Unisit USGA-101 sorption analyzer. A sample weight was placed in a fused-silica reactor and subjected to pretreatment, the samples were held at 375°C for 1 h in an argon stream and then cooled to room temperature under argon, after which a mixture containing 3.5% hydrogen in argon was passed through the reactor at a rate of 10 mL/min. The temperature was raised to 800°C at a rate of 8°C/min. The change in the thermal conductivity of the gas flow during the uptake of hydrogen by the sample was recorded using a thermal conductivity detector.

Catalytic experiments on the alkylation of aniline and hydroalkylation of nitrobenzene with methanol were conducted in a down-flow reactor under atmospheric pressure. Prior to the experiment the catalyst was activated in a hydrogen stream at 300°C for 30 min. The catalytic reaction was studied in the gas–liquid phase mode in a hydrogen stream at 300°C at reactants molar ratio aniline (or nitrobenzene) : methanol : hydrogen = 1 : 3 : 4.5 in a wide range of feedstock weight hourly space velocities of 5–100 h^{-1}.

Reaction products were determined using a gas–liquid chromatography technique on a Kristall 2000M chromatograph equipped with a flame ionization detector and a fused silica capillary column (30 m) coated with the SE-30 stationary phase and coupled gas chromatography–mass spectrometry on a Thermo DSQ-II instrument integrated with a Trace GC gas chromatograph equipped with an OV-101 coated fused silica capillary column (50 m). Chromatograms were recorded and processed using a Hewlett-Packard hardware–software complex. The catalytic properties of the samples were evaluated by aniline and nitrobenzene conversions and initial rates of product formation in the conversion range of 0–20%.

RESULTS AND DISCUSSION

Physicochemical Properties of Catalysts

The physicochemical characteristics of the samples: H-forms of various molecular sieves and copper-containing molecular sieves prepared via incipient wetness impregnation are given in Table 1. According to this data the introduction of copper in an amount of 7.5 wt % leads to a decrease in the pore volume by less than 20%.

Zeolites of four various structural types with the close Si / Al ratios, namely MOR, BEA, FAU (Y) and MFI were used in the study. The first three zeolites are molecular sieves with wide pores and channel diameters of 7.0 (MOR), 7.7 (BEA), and 7.4 (FAU) Å. Zeolite MOR has a pseudo-one-dimensional channel system with windows of main channels formed by 12-membered rings. Zeolites BEA and FAU (Y) have a three-dimensional channel system; the windows are formed by 12-membered rings along each of the three dimensions; there are also “supercages” of a 12 Å size in faujasite. Zeolite MFI possesses a three-dimensional channel system with 10-membered rings up to 5.5 Å in diameter and is related to mesoporous zeolites with medium-sized pores [21].

Table 1. Physicochemical characteristics of the catalysts

Sample	SiO_2/Al_2O_3 (mol)	V_{pore}, cm^3/g	$V_{micropore}$*, cm^3/g	Amount of desorbed NH_3, μmol NH_3/g
HFAU (Y)	60	0.45	0.24	357
HMOR	97	0.25	0.16	404
HMFI	80	0.23	0.14	564
HBEA	75	0.68	0.45	704
HMCM-41	50	0.88	1.32	417
Cu/FAU (Y)	60	0.40	0.21	664
Cu/MOR	97	0.20	0.13	826
Cu/MFI	80	0.19	0.10	893
Cu/BEA	75	0.55	0.15	871
Cu/MCM-41	50	0.75	1.03	936

* For HMCM-41 and Cu/MCM-41 samples is the mesopore volume calculated by the BJH method is presented.

All zeolites are characterized by the presence of two peaks on TPD NH_3 curves (Fig. 1): the low-temperature and the high-temperature peaks corresponding to weak acid sites and physisorbed NH_3 and strong acid sites, respectively. For all zeolite samples there is a prevalence of strong acid sites, they make more than 50% of total amount of acid sites. T_{max} of the high-temperature peak for zeolites is in the region of 350–460°C; by its value the initial zeolites can be arranged in the following row according to the strength of acid sites: FAU (Y) < BEA < MFI < MOR. The TPD NH_3 curve for MCM-41 is characterized by the presence of only one broad peak corresponding to weak acid sites and medium-strength acid sites with T_{max} in the temperature range of 170–250°C.

The modification of molecular sieve catalysts with copper nitrate leads to a change in the acidic characteristics of the samples. Figure 2 displays TPD NH_3 curves for the HFAU (Y) and Cu/FAU (Y) samples; the other catalysts reveal a similar dependence after modification with copper nitrate. The introduction of copper leads to the increase in the total amount of desorbed ammonia in the TPD NH_3 experiments for all the samples, with the strength distribution of acid sites altering as compared to the initial H-forms. The contribution of the low-temperature peak significantly increases, indicating an increase in the amount of weak and medium-strength acid sites, while the high-temperature peak observed at 450°C has a low intensity for all the samples. The decrease in the number of strong acid sites for zeolitic catalysts can be explained by the fact that ion exchange of zeolite protons for copper cations occurs during the impregnation. The appearance of an additional ammonia desorption peak at 320–350°C on the TPD NH_3 curves of copper-containing samples was also noticed. This peak corresponds to the decomposition of copper ammine complexes according to the authors of [22].

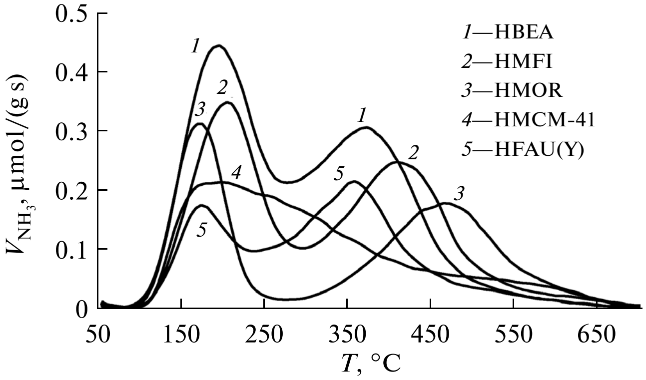

Fig. 1. TPD NH_3 curves for zeolites of various structural types and mesoporous material MCM-41.

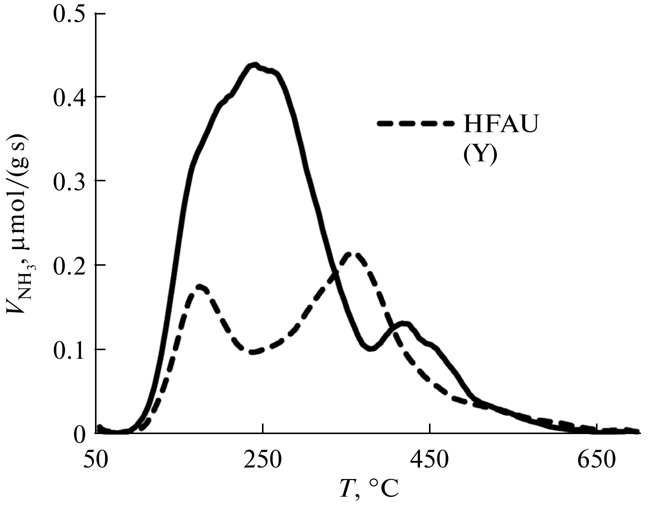

Fig. 2. TPD NH_3 curves for the HFAU (Y) and Cu/FAU (Y) samples.

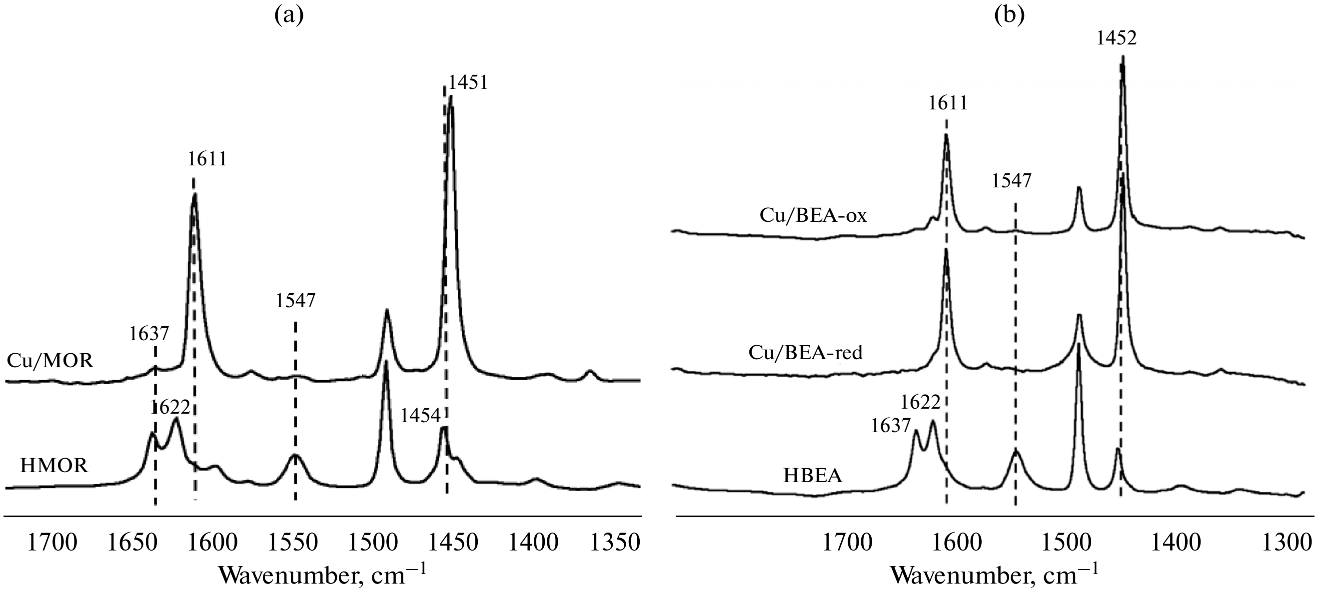

Fig. 3. IR spectra of pyridine adsorbed at 150°C on (a) HMOR and Cu/MOR and (b) HBEA and Cu/BEA.

The nature of the acid sites was studied using FTIR spectroscopy of adsorbed pyridine (Py). Figure 3 displays the IR spectra of Py adsorbed at 150°C on the samples of the initial and the copper-modified zeolites BEA and MOR; the spectra for other zeolites have a similar pattern. According to the FTIR data, part of zeolite protons is exchanged by Cu^+ cations after the impregnation with copper nitrate, this assumption is confirmed by an almost complete disappearance of the bands of pyridine fixed to Brønsted acid sites (1637 and 1547 cm^{-1}). While the intensity of the characteristic bands of pyridine adsorbed on Lewis acid sites (1622 and 1454 cm^{-1}) increases in case of Cu-containing samples and the band shifts to lower frequencies [23]. Thus a part of copper introduced by incipient wetness impregnation is embedded in the cation exchange positions, and the other part remains in the form of copper oxide, which is reduced to metallic copper during the treatment with hydrogen at 300°C, that is confirmed by TPR H_2 data (not presented in this paper). On the other hand, the exchanged Cu^+ ions are not reduced to Cu^0 during the in situ treatment with hydrogen at 300°C, and the band at 1547 cm^{-1} does not appear on the spectra of the reduced Cu/BEA sample (Fig. 3b).

Alkylation of Aniline with Methanol

The reaction of aniline alkylation with methanol was studied over various molecular sieves: zeolites BEA, FAU (Y), MOR and MFI and the mesoporous material MCM-41 as well as on the samples modified with 7.5 wt % copper. The catalytic properties were compared in terms of initial rates of products formation in the range of aniline conversion of 0–20%. The relative measurement error did not exceed 15%. Only *N*-methylaniline (NMA), *N,N*-dimethylaniline (NNDMA), and *p*-toluidine (T) were obtained as the products at low conversions. The H-forms of molecular sieves demonstrated rather low activity in alkylation at 300°C; the initial rates of product formation on the zeolite catalysts were close (Table 2). The initial formation rate of the desired product was two times higher over the mesoporous material MCM-41, but the selectivity towards *N*-methylaniline was noticeably lower; the predominant product was *N,N*-dimethylaniline. The formation of a large amount of the dialkylated product over MCM-41 can be explained by a larger pore size of this material.

The modification of the molecular sieve catalysts by introducing 7.5 wt % copper resulted in an increase in the alkylating activity by one to two orders of magnitude. This result can be associated with the increase in total acidity of the samples as well as with the change of the type of the acid sites, i.e., the increase in the contribution of medium-strength Lewis acid sites. It should be noted that the yield of *p*-toluidine as a product of C-alkylation on Cu-containing catalysts decreases, which may be due to a decrease in the quantity of strong Brønsted acid sites. These conclusions are in good agreement with the results of TPD NH_3 data and IR spectra of adsorbed pyridine. The catalyst Cu/MCM-41 demonstrated the highest activity; the initial rate of *N*-methylaniline formation over this catalyst was an order of magnitude higher than on Cu-containing zeolite catalysts. The zeolite catalysts can be arranged in accordance with alkylating activity as follows: Cu/MOR < Cu/BEA < Cu/FAU (Y) < Cu/MFI. The samples of Cu/MFI and Cu/MOR are

Table 2. Initial rates of products formation in aniline alkylation with methanol at 300°C, 5–100 h^{-1}, aniline : CH_3OH = 1 : 3 (mol)

Catalyst	Initial rate, mol × 10^{-9}/(g s)		
	NMA	NNDMA	T
HFAU (Y)	4.8	2.1	0.9
HMOR	4.2	1.5	0.3
HMFI	5.2	2.3	0.7
HBEA	4.5	1.8	0.2
HMCM-41	8.8	10.9	0.2
Cu/FAU (Y)	47.3	5.7	7.0
Cu/MOR	20.6	0.9	0.2
Cu/MFI	99.0	11.2	0.0
Cu/BEA	37.3	7.3	7.8
Cu/MCM-41	317.4	137.9	8.6

characterized by higher selectivity towards *N*-methylaniline.

Hydroalkylation of Nitrobenzene with Methanol

For catalytic experiments on the hydroalkylation of nitrobenzene with methanol were chosen three copper-modified molecular sieve catalysts that demonstrated the highest activity and/or selectivity in the aniline alkylation process. The data on the initial rates of formation of the main products: aniline, *N*-methylaniline and *N,N*-dimethylaniline are presented in Fig. 4. The best catalytic performance was demonstrated by the Cu/MCM-41 sample, which is in good agreement with the amount of active sites. The parameters of the nitrobenzene hydroalkylation with methanol over Cu/MFI and Cu/MOR were quite close, the catalysts exhibited similar activity in hydroalkylation. However, the highest selectivity for *N*-methylaniline (97%) among the alkylation products was demonstrated by the Cu/MOR sample. Cu/Al-MCM-41 showed rather high contribution of *N,N*-dimethylaniline (25%), most probably, due to the bigger pore size.

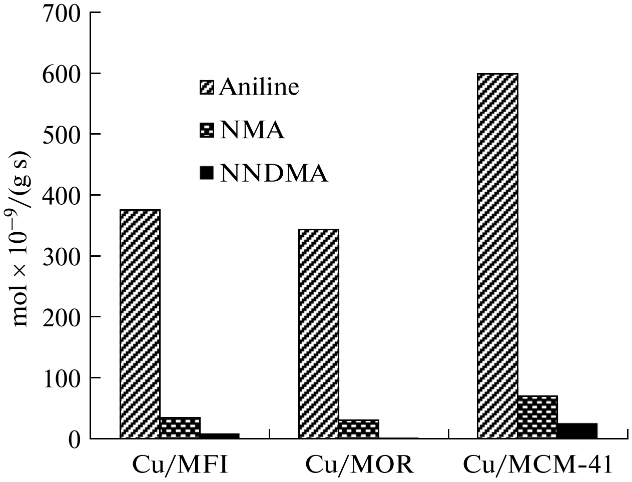

Fig. 4. Initial rates of products formation in nitrobenzene hydroalkylation with methanol at 300°C over various catalysts.

Also, the catalytic properties of Cu/MFI, Cu/MOR, and Cu/MCM-41 were compared under identical conditions: a temperature of 300°C and a feedstock weight hourly space velocity of 5.8 h^{-1}. The conversion of nitrobenzene was 74.1–99.9% over all the samples with aniline being the main product of the hydroalkylation of nitrobenzene, whereas the selectivity towards the desired product *N*-methylaniline reached only 7.4–13.4 mol %. The least amount of alkylation byproducts was obtained in case of Cu/MOR catalyst. The results of the experiments demonstrate that Cu-containing molecular sieves are promising catalysts for the one-step synthesis of *N*-methylaniline.

CONCLUSIONS

The aniline alkylation and nitrobenzene hydroalkylation reactions with methanol over copper-containing molecular sieves have been studied. In the investigation of the aniline alkylation process, it has been found that the modification with copper leads to enhancement of the alkylating ability of the catalysts based on molecular sieves; the initial rates of formation of the desired product *N*-methylaniline have increased by one to two orders of magnitude. It has been demonstrated that Cu-containing molecular sieves are effective catalysts for both aniline alkylation with methanol and the one-step synthesis of *N*-methylaniline from nitrobenzene and methanol. The catalyst Cu/MCM-41 exhibited the highest activity in the hydroalkylation of nitrobenzene, whereas the highest selectivity towards the desired product (97 mol %) among alkylation products was achieved over the Cu/MOR sample.

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