Studying the Catalytic Activity of Naturally Occurring Zeolites in the Gas-Phase Nitration Reaction of Aromatic Compounds

A. P. KOSKIN[1], K. S. GOLOKHVAST[2], I. G. DANOLOVA[1], A. A. VEDYAGIN[1,3] and I. V. MISHAKOV[1,3]

[1]*Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 5, Novosibirsk 630090 (Russia)*

E-mail: koskin@catalysis.ru

[2]*Far East Federal University, Ul. Sukhanova 8, Vladivostok 690950 (Russia)*

[3]*Novosibirsk State Technical University, Ul. K. Marksa 20, Novosibirsk 630092 (Russia)*

Abstract

An alternative gas phase nitration process was investigated wherein the reaction between an aromatic substrate (benzene/toluene) and a nitrating agent (either a 68 mass % HNO_3 aqueous solution, or a mixture of nitrous gases) occurs on a fixed-bed solid acidic catalyst. There have been studied physicochemical properties (elemental composition, pH, crystallinity) and catalytic properties inherent in the samples of naturally occurring zeolites taken from the deposits of Siberia and the Far East. An effect of zeolite preliminary treatment (calcination and acid extraction method) exerted on the activity thereof was investigated. It has been demonstrated that the highest activity is exhibited by a sample with the highest concentration of Bronsted acid sites (99 µmol/g according to NH3 adsorption), taken from the Kulikovo deposit (the Amur Region). The productivity of the sample amounted to161 mg/($g_{cat} \cdot$ h).

Key words: naturally occurring zeolites, acidic properties, gas-phase nitration of benzene, toluene, nitrobenzene, nitrotoluene

INTRODUCTION

For the last decades of the XX century in the manufacture of nitro compounds there has been a distinct trend outlined consisting in the fact that the explosives those were the main products of this industry during an entire century, began to give way to, compounds widely used in the production of polymeric materials and pharmaceutical preparations. The main volume of the releasing thereof (4–5 million t/year) falls at benzene and toluene nitro derivatives, and, first of all, at nitrobenzene and the mixture of dinitrotoluene isomers. These compounds have become a major source of raw materials for the production of polyurethane foam, one of the fastest developing industries of polymeric materials [1].

Despite a sesquicentennial history of the nitration process, the chemical and technological scheme thereof was not significantly changed. In the industry, this process is carried out in nitrators. The nitrating mixture consists of nitric acid, sulphuric acid and water at a ratio of 3 : 6 : 1, respectively. The molar ratio between HNO_3 and an aromatic compound generally amounts to 0.95–0.98 [2]. Sulphuric acid acts as a catalyst to activate nitric acid, and simultaneously as a diluent that accumulates the heat of the reaction and binds water un-

der formation. The process is carried out to until the H_2SO_4 concentration is reduced to a limiting value [3]. The mass of waste sulphuric acid (at a concentration of at least 70 %) amounts up to one ton per 1 t of commercial nitrobenzene. Thus, the presence of a great amount of concentrated sulphuric acid in the reaction medium and the fact that it is required for the circulation and utilization thereof result in significant instrumental and environmental difficulties.

Currently, efforts are underway to develop heterogeneous catalytic nitration processes for aromatic compounds. For example, the authors of [4] performed the liquid phase nitration of benzene (toluene) in the presence of catalysts based on alumina or silica-alumina impregnated with H_2SO_4 or H_3PO_4 (70 mass % of acid). The nitration process was performed in a solution of dichloromethane (CH_2Cl_2), using a 70–90 % solution of HNO_3 as a nitrating agent. The significant disadvantages of this approach consist in the periodicity of the process and the need of separating the catalyst from the reaction product.

Interest in the gas-phase nitration that allows avoiding many of the disadvantages of liquid-phase catalytic processes grew significantly during the past 20 years. This might be caused by the appearance of novel heterogeneous catalysts with strongly acidic properties those could compete with concentrated H_2SO_4. The nitration reaction proceeds *via* an acidic mechanism involving cation NO_2^+, therefore the catalyst in order to form NO_2^+ cation from the molecule of HNO_3 should have a sufficiently strong protonic acidity (greater than −3.0) [5]. The nitrating catalyst activity directly depends on the concentration and the strength of Brønsted acidic sites (BAC) on the catalyst surface. As a nitrating agent in the gas-phase process one uses HNO_3 or nitrogen oxides, which eliminates the problems associated with the regeneration of H_2SO_4 and purifying the sulphuric acid wastewater. Because of this the gas-phase nitration appears to be a more environmentally safe process. Another significant advantage of the gas-phase process consists in the opportunity of performing the process in a flow-through mode.

To date, a number of catalysts is known those were investigated in the nitration processes as applied to aromatic hydrocarbons and their derivatives. The first group of the catalysts in-

cludes oxide systems. The required increase of Bronsted acidity of metal oxides (Vb and VIb) can be achieved both either *via* sulphation (metal hydroxide impregnation with sulphuric acid and subsequent calcination) [6], or via the formation of mixed oxides. Binary oxide systems based on Mo, W, Ti, Zn, Zr, Sn, Al and Si, are most frequently used. The majority of such oxide systems can be attributed to solid superacids with the acidity level higher than the acidity of concentrated H_2SO_4 [6–10]. The most active and stable systems are presented by SO_4^{2-}/TiO_2 (80 %) + MoO_3 (20 %) [6] and 20 % MoO_3/SiO_2 [10].

Another type of catalysts for the gas phase nitration of aromatic compounds is obtained by applying sulphuric acid onto an inert carrier that does not collapse under the influence of acids (silica, silicon carbide, graphite, *etc.*). Despite a high activity of these systems, a significant disadvantage is inherent in them that consists in decreasing the stability of the catalyst due to leaching the sulphuric acid [11]. Adding a heteropolyacid in the catalyst composition can cause significantly increasing the operating lifetime thereof [12]. Japanese scientists proposed to use aromatic sulphonic acids for the nitration of benzene (for example, *o*-nitrobenzene sulphonic acid) applied onto silica gel [13].

The third group of catalysts consists of zeolites, layered clays and other aluminosilicates [6, 14–20]. It is known that the acidic properties of zeolites depend to a considerable extent on such factors as the type of zeolite, crystallinity thereof, the quantitative content of Si and Al therein, the presence of additionally introduced metal ions in the zeolite. As the result of preliminary heat treatment of zeolite at a temperature of 500–600 °C, mainly BAC are formed. At higher temperature values, the concentration of BAC decreases, whereas the concentration of the Lewis acidity centers increases, however, the role of the latter in the nitration reactions was not revealed until now [2]. The acidity of zeolites is affected by SiO_2/Al_2O_3 ratio. The range of Si/Al ratio in zeolites obtained by direct synthesis is severely limited. For changing the composition of zeolites they are exposed to a steam treatment or to aluminum acidic extrac-

tion from the crystal lattice. It should be noted that the undeniable advantage of the aluminosilicate catalysts consists in a relatively low cost and high selectivity thereof, including in the case of toluene nitration.

In the presence of heterogeneous catalysts, there is a real opportunity to influence the ratio between the resulting nitro isomers. The nitration reaction occurs on the surface of a solid catalyst, so the rate of hydrogen atom substitution in the aromatic ring by the nitro group depends on the nature of the catalyst and the mutual arrangement of the adsorbed molecules and the active sites responsible for the nitration reaction. For example, the authors of [18] demonstrated that in the presence of zeolites H-beta and ZSM-5 reaction proceeds with a high *para* selectivity level as compared with other catalysts those do not possess a microporous structure.

In this work, as the catalysts for the gas-phase nitration of aromatic compounds, we studied naturally occurring zeolites taken from the deposits of Siberia and the Russian Far East. The composition of the zeolites can be presented by the following empirical formula: $Me_{2/n}[(Al_2O_3)_x(SiO_2)_y] \cdot zH_2O$, where Me are the cations with the valency of n (Na, K, Mg, Ca, Ba, and others), the y/x ratio depends on the structure being generally within the range of 1−5. As it is known, mordenite, clinoptilolite and montmorillonite those form the structure of the majority of naturally occurring zeolites exhibit a high activity in the process under investigation [6, 15−17]. Among the physical and chemical parameters of naturally occurring zeolites determining the applicability thereof in catalysis, of most interest are porosity, sorption capacity, moisture content, acid-base properties and thermal stability. Of great importance is the resistance with respect to aggressive environments, because under such conditions there could occur the zeolite lattice destruction and, accordingly, the loss of catalytic activity.

As an additional problem, we analyzed the use of nitrous gases (NO_x, NO/NO_2) as a nitrating agent in the gas-phase nitration process. It is widely known that recycling these hazardous species represents an important environmental problem [21].

EXPERIMENTAL

Object of investigation

In the course of our work we investigated a series of zeolitized rocks sampled from different deposits in Russia: the Holino deposit (the Chita Region, clinoptilolite tuff, sample I), the Kulikovo deposit (the Amur Region, clinoptilolite-mordenite tuff, sample II), the Lyulino deposit (the Khanty-Mansi Autonomous District, clinoptilolite tuff, sample III), the Lyutog deposit (the Sakhalin Region, clinoptilolite tuff, sample IV), the Chuguyevo deposit (the Primorie Territory, clinoptilolite-mordenite tuff, sample V) and the Vangino deposit (the Amur Region, heulandite-clinoptilolite tuff, sample VI). All the zeolite samples were fractionated (0.25−0.5 mm), further they were converted into H-form by means of soaking in a 1 M HCl solution for 3 h and calcined within the temperature range of 300−600 °C. Samples II, IV were exposed to acidic modification (IIa and IVa, respectively), or they were treated according to the method of ion exchange which allowed us to vary the modulus of zeolitized species (Si/Al ratio), and the content of cations [15]. In addition, we studied two samples of naturally occurring zeolites with a high content of clinoptilolite taken from the Beliplast deposit (Bulgaria) and the Tsagaan Tsab deposit (southeast Mongolia), as well as a reference sample 15 mass % H_2SO_4/SiO_2, prepared according to a procedure described by the authors of [11].

Physicochemical properties of zeolites

The chemical composition of zeolitized rocks were analyzed by means of atomic adsorption spectroscopy (AAS) with the use of a Hitachi-180-50 spectrometer (Japan). The calculation of the modulus of zeolitized rocks (Si/Al ratio) was performed according to the AAS.

The acid-base properties were studied by means of IR spectroscopy using a Shimadzu FTIR8300 spectrometer (Japan). The total concentration of acidic sites in the samples was determined from the adsorption of NH_3 after preliminary calcination under vacuum at 450 °C

for 1 h. For this purpose, onto the sample at a room temperature there was adsorbed ammonia gas, to desorb the excess thereof after 15 min at 100 °C. The spectrum of adsorbed ammonia was registered at a room temperature. Further, we calculated the concentration of acidic centres (C) from the intensity of $\delta(NH_4^+)$ band of ammonium ion vibrations at 1450 cm^{-1}:

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

where A_0 is the coefficient of integral absorption cm/μmol ($A_0(NH) = 10$ cm/μmol [22]); ρ is the "thickness" of a tablet, g/cm^2; T_0, T − the transmittance of infrared radiation before and after the adsorption, respectively, %; ν is the wave number, cm^{-1}. The BAC concentration on the outer surface of the zeolite was determined from the adsorption intensity of CO. The calculation was performed basing on the intensities of the absorption band of OH groups in the H-complex with the CO molecule (the maximum being at $\nu_{(OH-CO)} = 3430{-}3450$ cm^{-1}) using the coefficient of $A_0(OH-CO) = 28$ cm/μmol. The concentration of BAC in the zeolite channels was determined from the intensity of OH group band in the H-complex with the CO molecule (the maximum being at $\nu_{(OH-CO)} = 3310$ cm^{-1}), using the coefficient of $A_0(OH-CO) = 57$ cm/μmol. The concentration of strong and weak Lewis acidic centers (LAC) was calculated from

the intensity of the absorption bands $\nu_{CO} = 2198{-}2202$ cm^{-1} and $\nu_{CO} = 2225{-}2230$ cm^{-1}, respectively.

The phase (mineral) composition of naturally occurring zeolites was determined by means of XRD method using an ARL X'TRA diffractometer (40 kV/mA). The phase identification was carried out using a PDF4+ database.

Catalytic activity

Installation for the gas-phase nitration of aromatic compounds. A schematic diagram of the installation for the gas-phase nitration of aromatic compounds is presented in Fig. 1. An organic substrate 1 (benzene, toluene) was supplied by means of an infusion pump (NIS-01, Russia) into an evaporator, thermostated at a temperature of 140−180 °C. Next, the substrate was fed into the mixer wherein it was mixed with a flow of the nitrating agent. The reaction was carried out within a flow-through reactor (material Pyrex glass, 10 mm diameter, 100 mm length) in an inert gas (nitrogen) flow. Then, the reaction mixture at the outlet of the reactor was cooled and the liquid components of the mixture were collected in a trap flask at 0 °C.
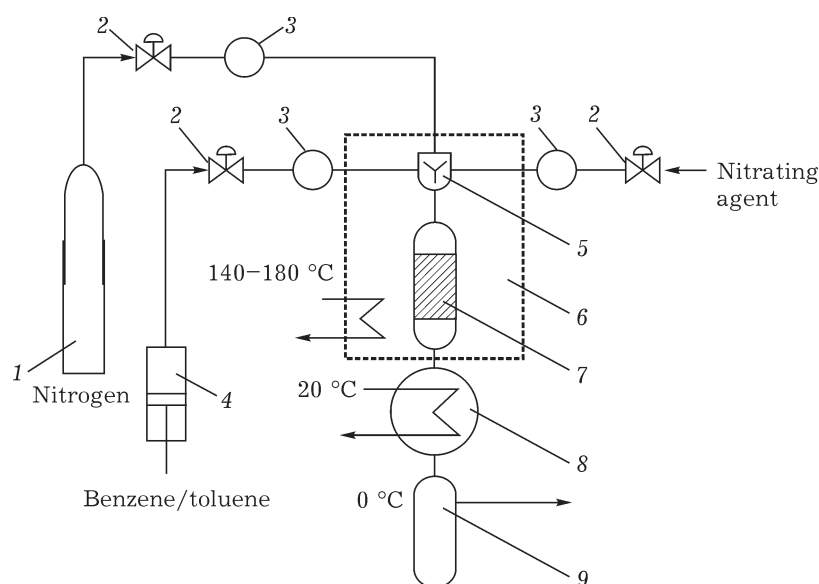

Fig. 1. Schematic diagram of the installation for the gas-phase nitration of aromatic compounds: *1* − pipeline of inert gas; *2* − stopcock, *3* − flow-rate meter, *4* − infusion pump, *5* − evaporator and gas-flow mixer; *6* − thermostated zone (140−180 °C), *7* − reactor, *8* − refrigerator for cooling the reaction mixture, *9* − trap for the liquid components of the reaction mixture.

We used two nitrating agents (NA). In the first case, we used an azeotropic aqueous solution of nitric acid (68 mass %, b. p. = 120 °C, density 1.40 g/cm^3). In the second case, the line of the azeotropic nitric acid solution was replaced by the line of nitrous gas NO$_x$ (NO/NO$_2$), preliminary obtained in a flow-through reactor *via* NO oxidation according to a procedure described by the authors of [23]:
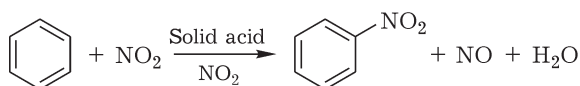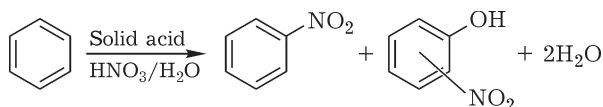
Gas-phase nitration of aromatic compounds. In the standard catalytic experiment, a weighed sample portion of zeolite equal to 2 g was loaded into the reactor. The flow rate of benzene (SV$_B$) was equal to 0.65 mL/(g$_{cat}$ · h), that of toluene being equal to (SV$_T$) 0.78 mL/(g$_{cat}$ · h), that azeotropic nitric acid (SV$_{NA}$) solution (68 mass %) amounting to 0.25 mL/(g$_{cat}$ · h), carrier gas (nitrogen) flow rate being equal to 3.5 L/h. The molar ratio of substrate/nitric acid was equal to 1.3 : 1. The experiment was conducted during 5 h. In order to study the deactivation of samples, the time of the experiment was increased up to 20 h using an increased contact load of reagents (SV$_B$ = 13, SV$_{NA}$ = 5 mL/(g$_{cat}$ · h)). The reaction mixture collected in the trap was separated from the inorganic phase to wash with an aqueous soda solution (1 mol/L). Further, an aliquot was taken from the organic phase for the chromatographic analysis. The concentration of nitrobenzene was determined by means of gas chromatography (a Crystal-2000M chromatograph, Russia, column HP-5, TCD), whereas the concentration of nitro-phenolic impurities was determined using high performance liquid chromatography (Agilent-1200 chromatograph, the USA, column SE-30, UVD). The loss of the organic substrate did not exceed 1 %. In the case of nitration with the azeotropic nitric acid solution we sampled from the inorganic phase an aliquot for the titrimetric determination of the amount of HNO$_3$ reacted (C_{NA}, %) to calculate the conversion level of nitric acid. Using the gas chromatography data, we calculated the catalyst productivity parameter STY$_{NB}$ (STY$_{NT}$), in mg/(g$_{cat}$ · h) as the mass of nitrobenzene (nitrotoluene) per unit of time, normalized to the mass of the catalyst. Increasing the value of STY$_{NB}$ (STY$_{NT}$) is accompanied by increasing the value of C_{NA}. Thus, both mentioned parameters could be used in order to assess the catalytic activity of the samples.

RESULTS AND DISCUSSION

Studying physicochemical properties of zeolites

At the first stage of the research work, naturally occurring zeolites from the Kholino,

TABLE 1

Averaged chemical composition of naturally occurring zeolites

Samples	Deposits	Oxide content for rock-forming elements, mass %				CL^a,	Si/Al^b
		(SiO$_2$ + Al$_2$O$_3$)	(Na$_2$O + K$_2$O)	(MgO + CaO)	Fe$_2$O$_3$	mass %	
I	Kholino	77.02	4.22	3.48	0.77	11.35	2.34
II	Kulikovo	82.07	4.52	1.73	2.47	8.84	3.21
III	Lyulino	73.07	1.85	7.00	4.28	13.08	2.10
IV	Lyutog	79.35	3.86	3.32	1.82	10.90	2.62
V	Chuguyevo	78.49	4.09	3.44	0.77	13.08	2.42
VI	Vangino	78.12	3.21	3.56	1.45	13.46	2.61
P-I	Beliplast	81.10	4.95	3.30	1.01	9.70	2.93
P-II	Tsagaan Tsab	79.00	5.02	3.17	1.83	10.10	2.68

^{a} CL − calcination loss.

^{b} The modulus of zeolite.

TABLE 2

Mineral composition of the samples of naturally occurring zeolites I−VI and P-I according to XRD, mass %

Phases	I	II	III	IV	V	VI	P-I
Zeolite (clinoptilolite/mordenite/stilbite)	70−80	80−90	30−40	60−65	70−80	30−40	95
Layered clay (montmorillonite)	5−10	0	5−10	5−10	5−10	30−40	0
Catalytically inactive phases (calcite, quartz, *etc.*)	10−15	10−20	50−60	10−15	20−30	20−30	5

Lyulino, Lyutog, Chuguyevo, Kulikovo deposits were studied by means of XRD and atomic absorption spectroscopy in order to determine the mineral composition and content of the rock-forming oxides, respectively. As it can be seen from Table 1, the molar ratio of Si/Al > 2 for all the samples. According to data reported in [2], only high-silica zeolites with a modulus of greater than 2 satisfy the requirements for practical use. Zeolites taken from the Kulikovo deposit are characterized by a maximum modulus.

According to the XRD phase analysis data (Table 2), samples I, II and V represent highly zeolitized tuffs with a total content of zeolite phases (clinoptilolite $(NaK)_4Ca[Al_6Si_{30}O_{72}] \cdot 24H_2O$, mordenite $(NaK)_8[Al_8Si_{40}O_{96}] \cdot 24H_2O$, stilbite $(NaK)_4Ca_8[Al_{20}Si_{52}O_{144}] \cdot 56H_2O$) greater than 70 mass %. Samples III and VI contain zeolite in a relatively low amount, not more than 40 mass %, but sample VI contains the phase of montmorillonite, that is also active in the case of gas-phase nitration reaction [24].

According to IR spectroscopy (Fig. 2), the samples of zeolites are characterized by a predominance of the identical types of OH groups: non-acidic terminal groups Si−OH ($\nu_{OH} = 3745$ cm^{-1}) and bridging Si−O(H)−Al groups, as well as OH groups ($\nu_{OH} = 3630$ cm^{-}
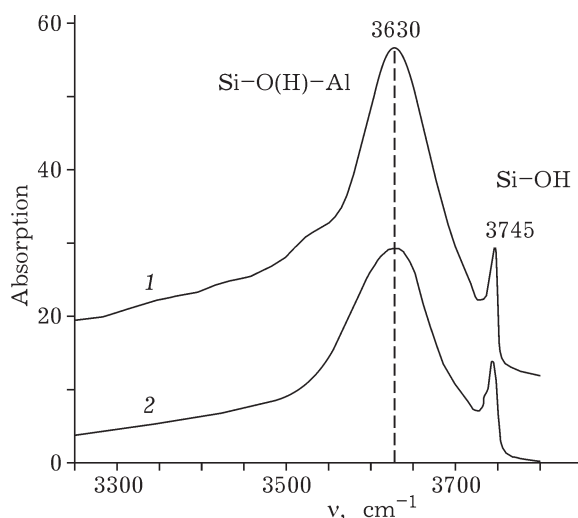

Fig. 2. IR spectra of the samples II (*1*) and IV (*2*) within the range of OH group vibrations.

[1]) bound with polyvalent cations. It should be noted that the BAC are predominantly located within the channels of the zeolites. Data concerning the concentrations of strong and medium-strength LAC (connected with Al^{3+}) for the samples of zeolites II and IV, determined by means of CO adsorption are presented in Table 3. From the data presented it follows that the concentration of the LAC and BAC is

TABLE 3

Total concentration of BAC and LAC, calculated from the adsorption of NH_3 and CO

Samples	Deposits	BAC concentration [$\delta(NH_4^+) = 1450$ cm^{-1}], μmol/g	LAC concentration, μmol/g	
			Al^{3+} (strong) ($\nu_{CO} = 2198-2202$ cm^{-1})	Al^{3+} (medium) ($\nu_{CO} = 2225-2230$ cm^{-1})
I	Kholino	37	−	−
II	Kulikovo	99	20	10
IV	Lyutog	45	2	3
V	Chuguyevo	49	−	−
VI	Vangino	52	−	−

Note. Here and in Table 4: dash denotes "not determined".

TABLE 4

Catalytic activity of the samples of naturally occurring zeolites in the nitration of benzene (STY_{NB}), mg/(g_{cat} · h)

Samples	Deposits	STY_{NB}	
		Nitrating agent	
		HNO_3/H_2O[b]	NO_x[c]
I	Kholino	32	2
II	Kulikovo	161	72
IIa	Kulikovo[a]	96	–
III	Lyulino	2	–
IV	Lyutog	51	37
IVa	Lyutog[a]	81	–
V	Chuguyevo	134	51
VI	Vangino	107	–
P-I	Tsagaan Tsab	151	68
P-II	Beliplast	157	70

Note. For designations see Table 3.

[a]Technique of acidic extraction for increasing the modulus of naturally occurring zeolite [15].
[b]Conditions of the process: reaction temperature 160 °C; SV_B = 0.65 mL/(g_{cat} · h).
[c]Conditions of the process: reaction temperature 180 °C; SV_B = 0.65 mL/(g_{cat} · h).

maximum for the samples taken from the Kulikovo deposit.

Gas-phase nitration of benzene

According to the results of catalytic tests, both in the case of using HNO_3/H_2O nitrating agent, and in the case of NO_x, we revealed the activity (Table 4 and Fig. 3) to depend directly on the Bronsted acidity of the samples (see Table 3): II > V > I. In the case of nitration with nitrogen dioxide, the yield of nitrobenzene was significantly lower. Thus, the results obtained are in a good agreement with the data from the literature [7].

Parameters STY_{NB} and C_{NA} are in a good correlation, except for sample III that exhibited a high value of C_{NA} (11.0 %) at a low value of STY_{NB}. This is, to all appearance, connected with a high content of iron in the zeolite formation. In this case, there could occur a partial reduction of the nitric acid by the components of naturally occurring zeolite. The catalytic activity of the rocks increases with increasing the Si/Al ratio and the crystallinity

level (for the fraction of the zeolite phase in the sample see Table 1).

The preliminary treatment of the zeolite samples studied was carried out in the two modes such as the treatment and acidic extraction, with further washing and calcination. This sequence of operations is presented in Fig. 4. Studying the influence of preliminary heat treatment upon the catalytic activity of naturally occurring zeolites demonstrated that after calcination at a temperature above 600 °C all the samples lose the catalytic activity. In the course of this treatment, there remain only the LAC those are low-active in the gas-phase nitration reaction [3]. In the absence of heat treatment, the catalytic activity of zeolites was insufficient for the reaction of gas-phase benzene nitration.

Two samples of naturally occurring zeolites taken from the Kulikovo and Lyutog deposits were modified using an acidic extraction method [15] in order to increase the Si/Al ratio (samples IIa and IVa, respectively). This technique included two procedures of acidic extraction by a 6 M HCl solution and subsequent calcination. The testing have demonstrated that in the case of Sample II this resulted in the reduction in the catalytic activity, to all appearance, as the result of a partial destruction of the
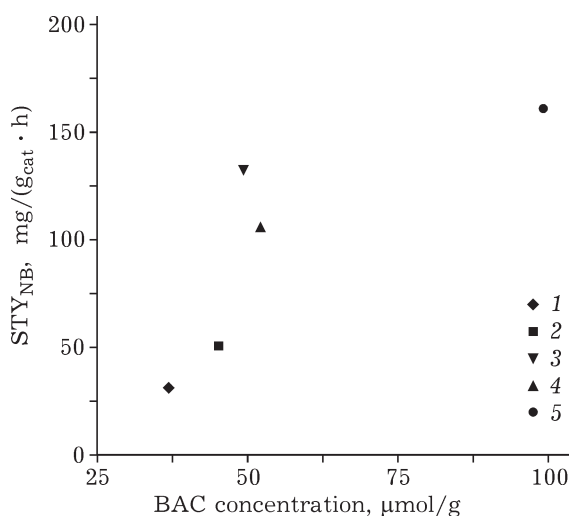

Fig. 3. Catalytic activity (STY_{NB}) of naturally occurring zeolites from different deposits depending on the concentration of Brønsted acidic centres (BAC): 1 – Kholino, 2 – Lyutog, 3 – Chuguyevo, 4 – Vangino, 5 – Kulikovo.

```
┌──────────────────────────┐              ┌──────────────────────────┐
│ Original zeolite         │              │ Original zeolite         │
│ (the Kulikovo deposit)   │              │ (the Lyutog deposit)     │
│ 3 h, 1 M HCl             │              │ 3 h, 1 M HCl             │
└──────────────────────────┘              └──────────────────────────┘
```

┌─────────────────────┐ ┌─────────────────────┐ ┌─────────────────┐   ┌─────────────────────┐
│ II-450 (450 °C)   │ │ II-600 (600 °C)   │ │ II-0   │   │ II-450 (450 °C)   │
│ C_{NA} = 27.1 %   │ │ C_{NA} = 12.4 %   │ │ C_{NA} = 13.7 %│   │ C_{NA} = 12.1 %   │
└─────────────────────┘ └─────────────────────┘ └─────────────────┘   └─────────────────────┘

┌──────────────────────────┐ ┌──────────────────────────────┐   ┌──────────────────────────┐
│ II-450-a   │ │ II-450-a2   │   │ IV-450-a   │
│ 16 h, 6 M HCl, 450 °C   │ │ 2 × 16 h, 6 M HCl, 450 °C   │   │ 6 M HCl, 450 °C   │
│ C_{NA} = 18.0 %   │ │ C_{NA} = 14.7 %   │   │ C_{NA} = 12.7 %   │
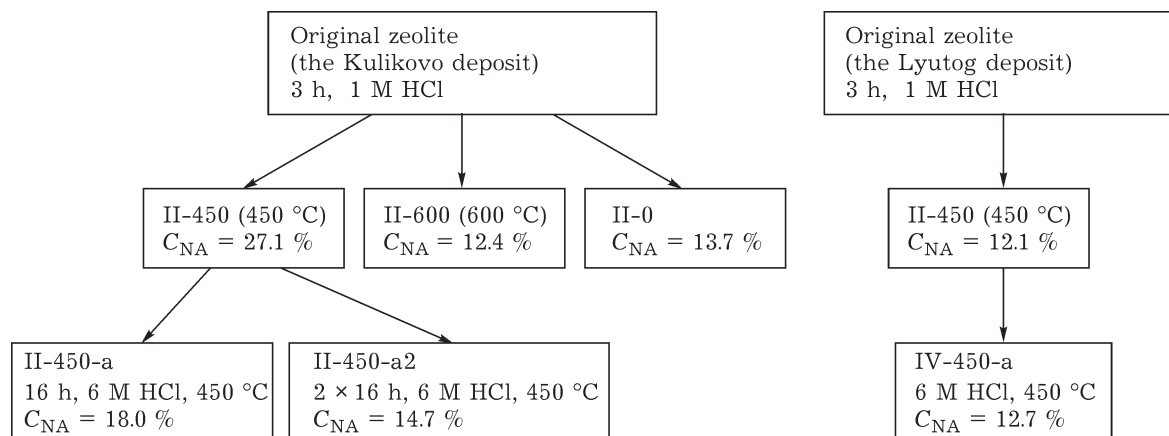└──────────────────────────┘ └──────────────────────────────┘   └──────────────────────────┘

Fig. 4. Catalytic activity of the samples of naturally occurring zeolites II and VI (the conversion level of nitric acid in the gas phase nitration reaction (C_{NA}, %) depending on the procedure of preliminary treatment.

zeolite framework (according to XRD phase analysis, the fraction of the zeolite phase ranged within 40−50 mass %). The catalytic activity of sample IV, that is more resistant to acidic treatment, exhibited a slight increase: STY_{NB} (IVa) = 81 mg/($g_{cat} \cdot$ h).

Gas-phase nitration of toluene

The gas-phase nitration of toluene was carried out under the same reaction conditions as the nitration of benzene. As nitrating agents, an aqueous solution of an azeotropic mixture of nitric acid and nitrous gases (NO_x) was used. The results of catalytic testing are demonstrated in Table 5. It is seen that the conversion level of toluene increases with increasing the Brønsted acidity of the samples. The selectivity level for the formation of different nitrotoluenes (*p*-NT/*o*-NT) in the reaction of nitration by

HNO_3 (the sum of *ortho* and *para* isomers) was amounted to about 99 %. The reaction by-products are presented by dinitrotoluene and benzaldehyde as a product of toluene oxidation. In the case of using the NO_x the selectivity level of nitrotoluene formation was higher. It should be also noted that the zeolites are characterized by a high selectivity level of para isomer formation. According to IR spectroscopy, the BAC are located mainly in the internal channels of the zeolite. The average diameter of the channels inherent in H-mordenite is equal to 6.3 nm. When the reaction of electrophilic substitution occurs in the zeolite channels, the *ortho* positions of the aromatic ring are difficult to access for the interact ion with NO_2^+.

TABLE 5

Gas-phase nitration of toluene

Samples	Deposit	STY_{NT}*, mg/($g_{cat} \cdot$ h)	*p*-HT/*o*-HT
P-III	−	352	1.84
II	Kulikovo	176	7.11
I	Kholino	50	6.90

* Process conditions: reaction temperature 160 °C; SV_T = 0.78 mL/($g_{cat} \cdot$ h).
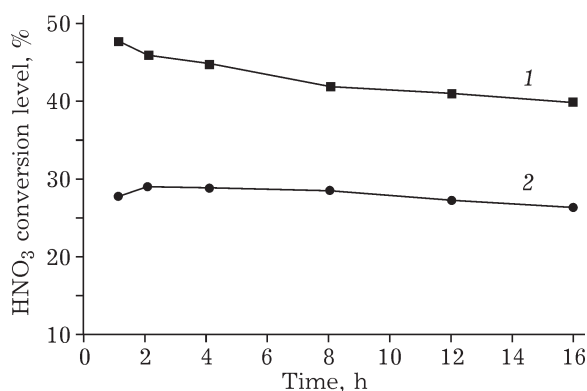
Fig. 5. Studying the stability of benzene nitration catalysts: *1* − reference sample P-III (15 % H_2SO_4/SiO_2), *2* − sample II (naturally occurring zeolite, the Kulikovo deposit).

Studying the stability of nitration catalysts

The stability of one of the most active catalysts for the gas-phase nitration of benzene, 15 mass % H_2SO_4/SiO_2 (sample P-III) [12], used as a reference sample, as well as that of naturally occurring zeolite from the Kulikovo deposit (sample II) was studied in the course of the gas-phase nitration of benzene. The activity was evaluated from the conversion level of nitric acid (azeotropic solution of HNO_3 as a nitrating agent, see Fig. 1). The results of the experiments presented in Fig. 5 demonstrate that the activity of the sample of P-III gradually decreases, whereas the naturally occurring zeolite is deactivated to a lesser extent.

CONCLUSION

The physicochemical and catalytic properties were studied concerning the gas-phase nitration reaction for a series of naturally occurring zeolites taken from the deposits of Siberia and the Far East. It has been demonstrated that the zeolite rocks could be considered as efficient catalysts for the gas-phase nitration of aromatic compounds due to the presence of mordenite, clinoptilolite and montmorillonite in the structure of the rocks. The catalytic activity of zeolite increases with the crystallinity level of the rock, the Bronsted acidity and the modulus of the zeolite. The advantages of these materials consist in a low cost thereof, a high selectivity with respect to the nitration product and an acceptable stability in operation.

REFERENCES

1 Zhilin V. F., Zbarskiy V. L., *Ros. Khim. Zh.*, L (2006) 104.
2 Greysh A. A., *Ros. Khim. Zh.*, 48, 6 (2004) 92.
3 Bakhvalov O. V., *Chem. Sustain. Dev.*, 11, 3 (2003) 449. URL: http://www.sibran.ru/en/journals/KhUR
4 US Pat. No. 3928476, 1975.
5 Ivanov A. V., Kustov L. M., *Ros. Khim. Zh.*, XLIV (2000) 21.
6 Sato H., Nagai K., Yoshioka H., Nagaoka Y., *Appl. Catal. A: Gen.*, 175, 1−2 (1998) 209.
7 Sato H., Hirose K., *Res. Chem. Intermed.*, 24, 4 (1998) 473.
8 Sato H., Hirose K., *Appl. Catal. A: Gen.*, 174, 1?2 (1998) 77.
9 Greysh A. A., Demygin S. S., Kustov L. M., *Kataliz v Prom.*, 4 (2002) 4.
10 Umbarkar S. B., Biradar A. V., Mathew S. M., Shelke S. B., Malshe K. M., Patil P. T., Dagde S. P., Niphadkar S. P. and Dongare M. K., *Green Chem.*, 8 (2006) 488.
11 Chen J. L., Cheng W. G., Liu H. F., Lin Q. S., Lu L. H., *Chinese Chem. Lett.*, 13, 4 (2002) 311.
12 Zhou P., Wang X. P., Cai T. X., *Chinese Chem. Lett.*, 13, 10 (2002) 1013.
13 Japan Pat. No. 01-287063, 1989.
14 EU Pat. No. EP 0551052, 1993.
15 Bertea L. E., Kouwenhoven H. W., Prins R., *Appl. Catal. A: Gen.*, 129, 2 (1995) 229.
16 RU Pat. No. 2087463, 1997.
17 Bertea L. E., Kouwenhoven H. W., Prins R., *Stud. Surf. Sci. Catal.*, 84 (1994) 1973.
18 Vassena D., Kogelbauer A., Prins R., *Catal. Today*, 60, 3−4 (2000) 275.
19 Yurkov V. V., Lankin S. V., Baryshnikov S. V., Kolesnikova L. G., Rogulina L. I., Serov A. V., *Vestn. DVO RAN*, 1 (2004) 69.
20 Choudary B. M., Sateesh M., Lakshmi Kantam M., Koteswara Rao K., Ram Prasad K. V., Raghavan K. V., Sarma J. A. R. P., *Chem. Commun.*, 1 (2000) 25.
21 Leonov V. T., Nauchnye i Tekhnologicheskiye Osnovy Utilizatsii i Pererabotki Oksidov Azota iz Otkhodov Gazov (Author's Abstract of Doctoral Dissertation in Engineering), Moscow, 2009.
22 Paukshtis E. A., Infrakrasnaya Spektroskopiya v Geterogennom Kislotno-Osnovnom Katalize, Nauka, Novosibirsk, 1992.
23 Irfan M. F., Goo J. H., Kim S. D., *Appl. Cat. B: Env.*, 78 (2008) 267.
24 EU Pat. No. EP 949240, 1999.