

Synthesis of ZSM-5 galloalumosilicate and investigation of their physicochemical and catalytic properties in the course of conversion of propane into aromatic hydrocarbons

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Abstract. Galloalumosilicates having ZSM-5 structure are manufactured from the alkali alumina silica gels via the method of hydrothermal crystallization using different organic templating agents. Their physico-chemical and acidic properties are investigated and their catalytic reactivity is determined in the course of propane conversion into aromatic hydrocarbons. The highest catalytic reactivity and stability are exhibited by the Ga-containing zeolite synthesized using hexamethylenediamine as a structure-forming additive.

1. Introduction

Zeolite catalysts modified with various metals are widely used in different industries. A promising method for modification of zeolites aimed to improve their properties is the introduction of metal cations into their framework at the stage of hydrothermal synthesis.

The elemento-aluminosilicates prepared by this method differ from the unmodified zeolites in their physicochemical properties directly controlled by the structure of the framework aluminosilicate [1-3]. The peculiarity of the synthesis of zeolites having ZSM-5 structure consists in the fact that the hydrothermal crystallization of aluminosilicagel is conducted in the presence of different organic compounds (templates). During the synthesis as the crystals grow the molecules of organic templates penetrate into the solid phase providing a stabilization of zeolite structure. The morphology and composition of the zeolite crystals of a certain structure could be modified using a number of structure-forming agents [4-5].

The aim of this work is to study the mechanisms of conversion of propane into aromatic hydrocarbons over ZSM-5 galloalumosilicates prepared using a variety of organic templates.

2. Experimental

Galloalumosilicates were prepared by isomorphous substitution of Si (IV) with Ga (III) in the zeolite crystal lattice at stage of hydrothermal synthesis via partial substitution of aluminum with gallium in the initial aluminum silica gel ($\text{SiO}_2/\text{Al}_2\text{O}_3+\text{Ga}_2\text{O}_3 = 40$). The liquid glass composed of 9% Na_2O , 29% SiO_2 , and 62% H_2O was the source of silicon, while solutions of alumina and gallium nitrates were used as sources of their oxides. Hexamethylenediamine (HMDA), diethylenetriamine (DETA) and urea (carbamide) were used as templates. The content of gallium oxide in the catalysts was 1.85 wt%. The resulting reaction mass was crystallized in steel autoclaves at 170 °C for 4 days. The crystallization completed, the solid phase was separated from the liquid phase by filtration, washed



with distilled water until the wash water $\text{pH} \leq 9$ was reached, and then air-dried at 110°C and calcined at 540°C for 16 hrs.

To convert the zeolites to the active H-form, the samples were treated with a 25% aqueous NH_4Cl solution at 90°C for 2 hours. After removal of the sodium cations, the zeolite samples in the NH_4 -form were dried at 110°C and air-calcined at 540°C for 6 hrs.

The quality of the resulting samples was controlled by IR spectroscopy and XRD analysis. IR spectra for the samples under study were recorded from the zeolite pellets using a FT-IR Nicolet 5700 spectrometer within the range of $2000\text{--}400\text{ cm}^{-1}$ in the presence of KBr (1.2 mg of high silica zeolites per 300 mg of KBr) in air. An XRD analysis of samples was performed in a DRON-3M X-ray apparatus (Cu-anode, Ni-filter).

The morphology and size of the zeolite crystals were determined using the method of scanning electron microscopy (SEM). SEM images were obtained on a LEO EVO 50 apparatus (Zeiss, Germany) at the Nanotech shared use center of the Institute of Strength Physics and Materials Science SB RAS.

The acidic properties of the catalysts were tested by the method of temperature-programmed desorption (TPD) of ammonia. The TPD experimental procedure was described in [6]. The concentration of the acid sites in the investigated samples was determined by the amount of ammonia desorbed at the moment of identification of desorption peaks and expressed as micromoles per 1 g of the catalyst.

The parameters of porous structure and a specific surface area of the samples were determined by the Brunauer, Emmett, Teller (BET) method using a TriStar II (3020) automatic gas adsorption analyzer (Micromeritics, USA). The specific surface area was calculated from the adsorption isotherms for nitrogen at 77 K. The volume and pore size of samples were determined by BJH (Barett-Joyner-Halenda) model from the data on adsorption and desorption isotherms at a relative pressure $P/P_0 = 0.99$.

The experiments for studying the process of propane conversion into aromatic hydrocarbons were carried out in a test flow-type reactor at atmospheric pressure, at the reaction temperature of $400\text{--}600^\circ\text{C}$ and the volumetric feed rate of feedstock 500 hr^{-1} .

The reaction products were analyzed by GLC using a Khromatek-Kristall 5000.2 chromatograph. The volume of the catalyst fed into the reactor was 3.0 cm^3 and its particle size was within $0.5\text{--}1.0\text{ mm}$. The catalytic activity of the samples was estimated from the propane conversion data. The yield and formation selectivity of the gaseous and liquid products were also calculated.

3. Results and Discussion

The results of X-ray studies showed that all samples synthesized correspond to the structure of ZSM-5 zeolite and belong to the orthorhombic syngony system. Figure 1 shows the IR spectra for the resulting galloalumosilicates, indicating the presence of absorption bands characteristic of ZSM-5 zeolites [7]. The samples exhibit absorption bands in the region $550\text{--}560\text{ cm}^{-1}$ attributed to oscillations of the tetrahedra, $[\text{SiO}_4]$ and $[\text{AlO}_4]$, over the external constraints of the skeleton due to the presence of four-, five- and six-member double rings, which determine their structure. The ratio of the intensities of the absorption bands at 550 and 450 cm^{-1} allows us to estimate the purity of the samples synthesized and the degree of their crystallinity.

For the Ga-containing zeolite synthesized with urea, this ratio is less than 0.6, which indicates a low degree of its crystallinity. The crystallinities of the Ga-containing zeolites prepared using HMDA and DETA are found to be 89 and 100%, respectively.

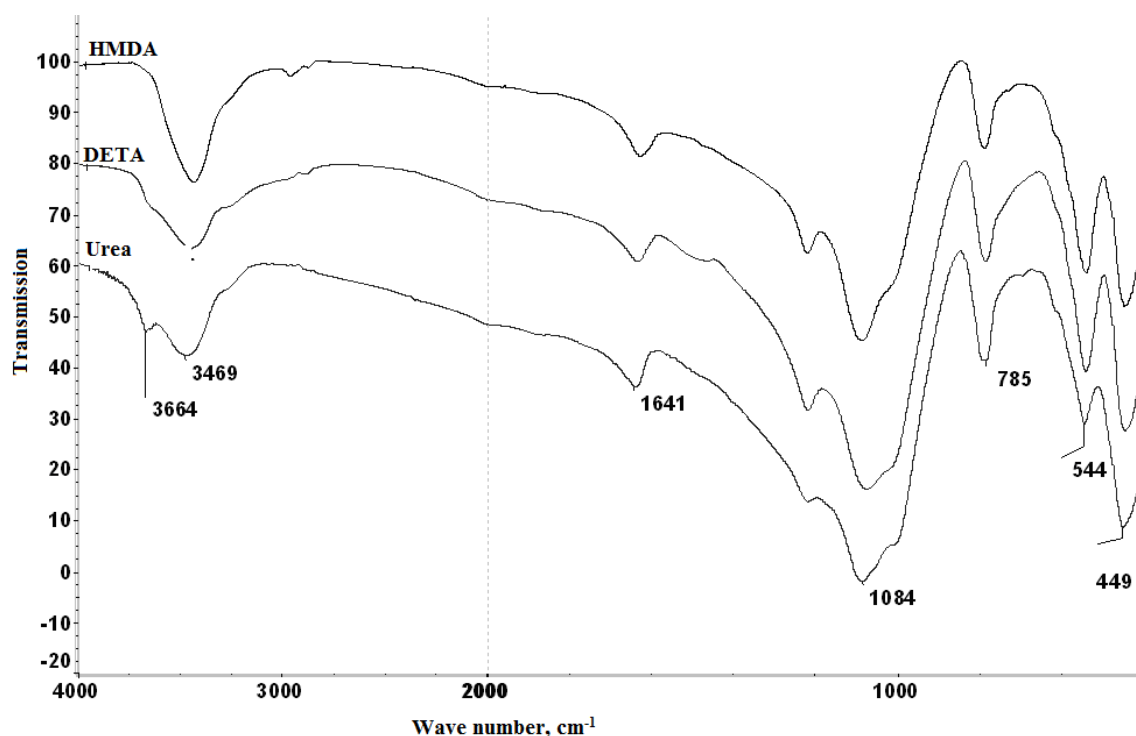


Figure 1. IR spectra of galloalumosilicates.

According to data of microscopic examination the morphology and size of the particles of zeolites synthesized with various structurants are significantly different (figure 2). The particles of zeolite prepared with HMDA have a sphere-like shape (single crystals) and are characterized by a highly-developed surface area. The sizes of the spheroids are within 3-8 microns. The use of urea as a structure-forming additive in the zeolite synthesis the urea results in the formation of finely-faceted isolated crystals in the shape of hexagonal prisms with the faces measuring 3-5 microns. The particles of zeolite synthesized with DETA have the shape similar to that of zeolite particles prepared with HMDA, but their grain sizes are quite different: there are both small and large crystals. An addition of HMDA in the stage of hydrothermal synthesis results in the formation of multiple nuclei, while the synthesis of zeolite using urea gives rise to the formation of a small number of zeolite nuclei during aging of aluminosilicagel. This suggests two mechanisms of synthesis of zeolites differing in their induction periods and leading to the formation of crystals with different morphologies.

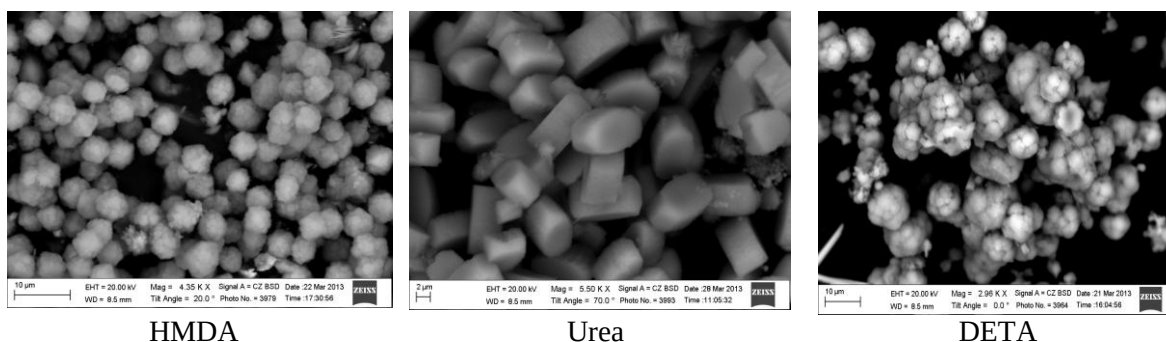


Figure 2. SEM images of galloalumosilicates prepared with different structure-forming agents.

An important characteristic of zeolite catalysts, determining their activity in various chemical reactions are their acid-base properties. To investigate the acidic properties of gallium-containing zeolites use was made of an ammonia probe due to a high basicity of ammonia, small size of its molecule, and the ease of its dosage, which allowed us among other things to determine not only strong but also weak acidic sites. In order to avoid the physical adsorption of ammonia, it was adsorbed over the samples at a temperature of 100 °C. The data on studies of acidic properties of prepared gallium-containing zeolites are presented in table 1.

Table 1. Acidic properties of gallium-containing zeolites.

Template	T _{max} , °C		Concentration, μmol/g		
	T _I	T _{II}	C _I	C _{II}	C _Σ
HMDA	200	425	649	298	947
DETA	210	415	621	267	888
Urea	215	420	605	314	919

Note. T_I, T_{II} are the temperatures of maxima of low- and high-temperature peaks on the thermal desorption curves; C_I, C_{II} and C_Σ are the concentrations of weak and strong acid sites and their sums, respectively.

All prepared samples possess acid sites of two types as evidenced by the presence of two ammonia desorption types in the thermal desorption spectrum: weak and strong acid sites with the maximum peak temperatures, T_{max} = 200-215 °C (I) and T_{max} = 415-425 °C (II), respectively. The use of urea as a template in the synthesis of galloalumosilicate results in the formation of a zeolite with the lowest concentration of weak acid sites that are characterized by a higher strength. The galloalumosilicate synthesized using HMDA contains the maximum number of acid sites, whose total concentration is 947 μmol/g, while the galloalumosilicate synthesized using DETA has the minimal number of high-temperature acid sites characterized by a lower strength. Thus, the investigation of acidic properties of the galloalumosilicates has shown that they are characterized by different distributions and ratios of acid sites of different nature, which affects their catalytic properties in the conversion of propane into aromatic hydrocarbons.

An investigation of the structural properties of galloalumosilicates has shown that the samples synthesized using HMDA and DETA have nearly the same specific surface areas and the total pore volume of the second sample is 0.024 cm³/g only, which is 3.75 times smaller than that of the galloalumosilicate sample synthesized with HMDA. The galloalumosilicate prepared with urea has the largest average pore size but the lowest value of the specific surface area (table 2). This in turn has an influence on the activity and selectivity of the samples during the propane aromatization.

Table 2. Structural properties of galloalumosilicates.

Template	S _{spec} (BET), m ² /g	Total pore volume, cm ³ /g	Average pore size, nm
DETA	303	0.024	3.4
HMDA	313	0.09	5.0
Urea	240	0.04	7.1

The investigation of catalytic properties of resulted galloalumosilicates has shown that they differ from each other in the total (measured by propane conversion degree) and aromatizing reactivities. The highest reactivity in the reaction of aromatization of propane is exhibited by the galloalumosilicates synthesized using HMDA and DETA (table 3). The sample synthesized with DETA exhibits a higher activity at the reaction temperatures 400-500 °C, while at 600 °C there is a decrease both in the conversion of propane and in the yield of aromatic hydrocarbons, which is probably due to the low stability of the catalyst performance. The sample synthesized using HMDA

exhibits a high catalytic activity at the temperatures 550 and 600 °C. The lowest aromatization activity is exhibited by the catalyst sample prepared using urea. A 76% propane conversion over this catalyst results in a 43.2% yield of aromatic hydrocarbons at the process temperature 550 °C. An increase in the temperature to 600 °C leads to a significant decrease in the catalyst activity, which is apparently due to the presence of a large number of strong acid sites on its surface, which are directly involved into the reactions resulting in the formation of carbon deposits and rapid catalyst deactivation. The reaction product formed over this catalyst at a reaction temperature of 600 °C contains a large number of lower C₂-C₄ olefins.

Table 3. Characteristic of the products of propane conversion over gallium-containing zeolites.

Template	T _{reaction} , °C	X, %	A, %	S _{ar} , %	S _{cr} , %	S _{dehydrogen} , %	S _{H₂} , %
HMDA	400	11	1.6	14.5	74.9	5.8	4.8
	450	26	4.3	16.5	68.0	7.6	7.9
	500	66	36.7	54.3	36.6	4.6	4.6
	550	92	51.9	56.7	35.1	4.0	4.3
	600	97	51.0	52.5	37.7	5.4	4.4
DETA	400	15	2.2	14.2	77.0	3.0	5.8
	450	38	6.7	17.9	71.9	3.3	6.9
	500	81	49.1	60.3	34.1	1.9	3.6
	550	92	50.8	55.1	37.9	2.8	4.3
	600	70	37.0	52.9	26.6	15.9	4.5
Urea	400	11	1.7	15.9	73.6	4.8	5.7
	450	26	5.1	19.3	67.5	5.8	7.5
	500	61	31.9	52.0	39.2	4.2	4.5
	550	76	43.2	56.7	32.5	5.6	4.2
	600	26	7.6	29.8	19.2	47.8	3.3

Note. X is the propane conversion; S_{ar}, S_{cr}, S_{dehydrogen} is the selectivity by aromatisation, cracking, and dehydrogenization, respectively; S_{H₂} is the selectivity towards a formation of hydrogen; A is the yield of aromatic hydrocarbons.

The major liquid products of propane conversion over Ga-containing zeolite catalysts are aromatic hydrocarbons consisting mainly of benzene, toluene, alkylbenzenes, and aromatic compounds with higher molecular weight including naphthalene, methyl- and dimethylnaphthalenes. Byproducts are represented by gaseous hydrocarbons – methane and ethane. Hydrogen and C₂-C₄ olefins are present in minor amounts. Minor content of olefins in the reaction products suggests that they are intermediates that are actively involved into further interactions, resulting in the formation of aromatic compounds. Fig. 3 presents data on the influence of the template nature on the composition of the liquid products of propane conversion over Ga-containing zeolites. It should be noted that a sufficiently large amount of monoaromatic hydrocarbons (benzene, toluene, xylene etc.) is formed over all catalysts under study. Their fraction in a liquid product is higher than 60%. The lowest amounts of naphthalene and its derivatives were produced on the galloalumosilicate synthesized with an addition of urea. Thus, the use of different templates for the synthesis yields the samples differing in their catalytic properties.

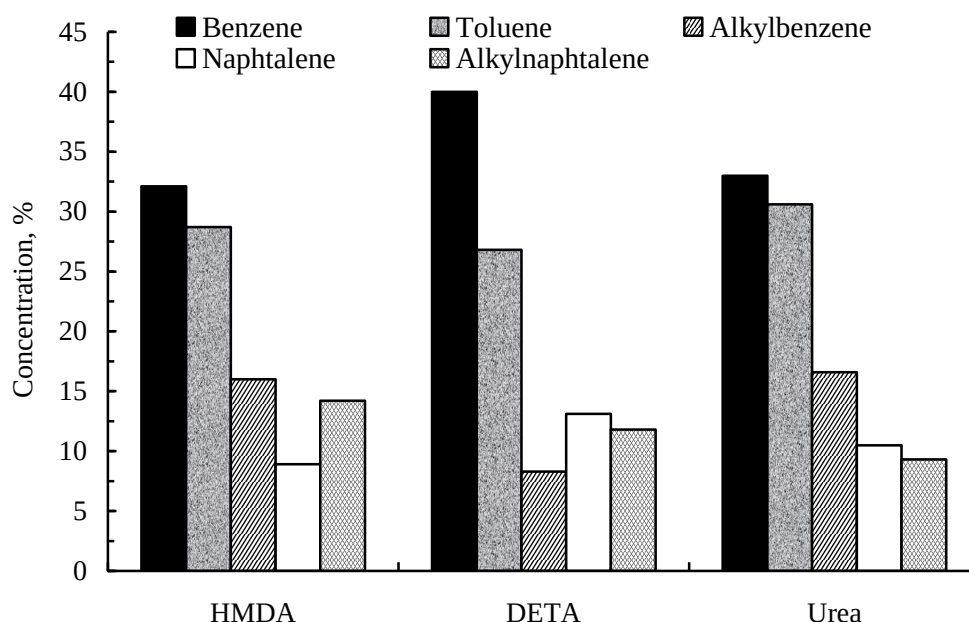


Figure 3. Composition of liquid products of propane conversion over Ga-containing zeolites synthesized using HMDA, DETA, and urea as templates ($T = 600\text{ }^{\circ}\text{C}$).

4. Conclusion

The investigation of activity of Ga-containing ZSM-5 zeolites in the course of conversion of propane into aromatic hydrocarbons has shown that the nature of a structure-forming organic agent used in the synthesis is very important. The most active catalytic reactivity has been exhibited by the Ga-containing zeolite prepared using hexamethylenediamine as an additive. The conversion of propane over this catalyst at $550\text{ }^{\circ}\text{C}$ and 500 h^{-1} has been found to be 92%, while the yield and selectivity towards the formation of aromatic hydrocarbons – 51.9% and 56.7%, respectively.

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