

Aromatization of Propane over Element-Alumosilicate Catalysts with ZSM-5 Structure

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Abstract. A method of hydrothermal crystallization of alkaline aluminosilicagels is used to manufacture element-aluminosilicates with ZSM-5 structure. Their physicochemical and acid properties are investigated and their catalytic activity in the course of propane conversion to aromatic hydrocarbons is determined. The Ga-aluminosilicate is found to be the most efficient zeolite catalyst for propane aromatization.

1. Introduction

High-silica zeolites are widely used as catalysts in oil refining and petrochemistry. A combination of their unique structural and acidic properties with a dehydrogenation ability of the promoting additives makes it possible to manufacture effective catalysts for aromatization of light hydrocarbons, in particular, propane. To increase the selectivity of aromatization, a chemical or thermal modification of high-silica ZSM-5 zeolites is used. Typically, zeolites are modified by the methods of ion exchange and impregnation with solutions of metal salts, mechanical mixing with metals or their oxides, and isomorphous substitution of aluminum in the crystal lattice for other elements [1-2, 4]. A partial or complete substitution of aluminum ions in the aluminosilicate lattice for cations of other metals is an effective way of controlling the properties of zeolites aimed at changing their activity and selectivity. The element-aluminosilicates (EAS) formed in this case preserve the structure of the respective zeolite; they however possess a number of individual features due to the origin of ions constituting the zeolite skeleton [3].

The aim of this work is to study the mechanisms of propane aromatization over an ZSM-5 element-aluminosilicates.

2. Experimental

An aluminosilicate (AS) with a silica modulus (M) 40 was synthesized under hydrothermal conditions from the alkali alumina silica gels using hexamethylenediamine (HMDA) as an organic additive. The liquid glass composed of 29% SiO₂, 9% Na₂O, and 62% H₂O was the source of silicon and Al(NO₃)₃ 9 H₂O was the source of aluminum.

The AS was synthesized using HMDA by the following procedure: aqueous solutions of HMDA and aluminum salts were added to the liquid silica glass under vigorous stirring. The pH of the reaction mixture was controlled by adding a 0.1 N solution of the nitric acid.

The resulting reaction mass was crystallized in steel autoclaves at 170 °C for 4-5 days. The crystallization completed, the solid phase was separated from the liquid phase by filtration, washed



with distilled water until the wash water pH ≤ 9 was reached, and then air-dried at 110 °C and calcined at 540 °C for 16 hrs.

Gallium- and indiumalumosilicate (Ga-AS and In-AS) were synthesized by the same method via partial substitution of aluminum with gallium or indium in the initial ($\text{SiO}_2/\text{Al}_2\text{O}_3 + \text{Me}_2\text{O}_3 = 40$) aluminum silica gel. The content of gallium and indium oxides was 1.85 and 1.82 wt%, respectively.

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 and XRD. The IR spectra were recorded from the zeolite pellets using a FT-IR Nicolet 5700 spectrometer within the range of 2000–400 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 acidic properties of the catalysts were tested by the method of temperature-programmed desorption (TPD) of ammonia. The TPD method allows the energy spectrum of the catalyst to be recorded from adsorption of the probing substance and the concentrations of active sites to be quantified for different desorption types. The TPD experimental procedure was described in [5]. 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. Ammonia was selected as an adsorbate for two reasons: its high basicity that allows determining not only the strong acid sites but also weakly acid ones and its small molecular size and simple dosing.

The activity of catalysts studied was investigated in the course of propane conversion into aromatic hydrocarbons in a flow-type reactor with a fixed-bed catalyst ($V_{\text{cat}} = 3 \text{ cm}^3$) at atmospheric pressure at the reaction temperature 400–600 °C and the feed space velocity 500 h^{-1} . The reaction products were analyzed by GLC using a Khromatek-Kristall 5000.2 chromatograph. To determine the composition of the liquid phase, use was made of a BP-1 PONA capillary column (100 m x 0.25 mm x 0.5 mm) and the gas-phase compositions were determined in the GS-Gas-Pro (60 m x 0.32 mm) capillary and Carbosieve S-II (4 m x 2 mm, 60/80 mesh) packed columns. 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 data on the composition and degree of crystallinity of elementoalumosilicate synthesized are presented in table 1.

Table 1. Composition and crystallinity of elementoalumosilicate.

Sample	Concentration, %		Molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 + \text{Me}_2\text{O}_3$	Degree of crystallinity, %
	Me_2O_3	Al_2O_3		
AS	–	4.07	40	100
Ga-AS	1.85	3.01	40	97
In-AS	1.82	3.34	40	95

The results of X-ray studies showed that all samples synthesized correspond to the structure of ZSM-5 zeolite and belong to the rhombic system.

Figure 1 shows the IR spectra for the resulting element-alumosilicates, indicating the presence of absorption bands characteristic of high-silica zeolites. All samples exhibit absorption bands in the region 550–560 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

determines their structure. The zeolites synthesized are characterized by a high degree of crystallinity that is somewhat reduced by an addition of gallium and indium, which is probably due to the slowing crystallization of silicate ions in the presence of gallium or indium ions (table 1).

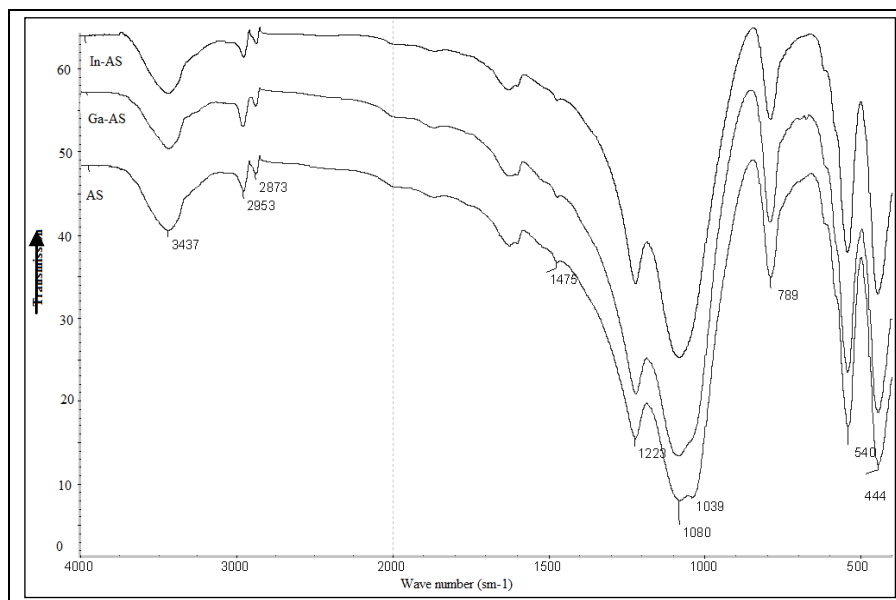


Figure 1. IR spectra for element-alumosilicates.

An important characteristic of zeolite catalysts, determining their activity, are their composition-controlled acid-base properties. The data on acid property studies are presented in table 2. An aluminosilicate possesses acid sites of two types as evidenced by the presence of two ammonia desorption types in the thermal desorption spectrum: weak acid sites with the temperature of peak maximum $T_{\max} = 205$ °C and strongly acidic with $T_{\max} = 425$ °C. The concentration of weakly acid sites is 676 $\mu\text{mol/g}$ and that of strong acid sites – 251 $\mu\text{mol/g}$ (table 2).

An introduction of gallium into the zeolite in the course of hydrothermal synthesis results in a change in its acidic properties, primarily, an increase in the strength and concentration of weak acid sites. The reason is that the new stronger active sites with a high energy of ammonia retention are formed by the introduction of gallium into the zeolite. The formation of strong aprotic acid sites that contain gallium atoms results in an increased activity of galloalumosilicates in reactions of aromatization of lower alkanes, since their formation is accompanied by a sharp increase in the rate of the limiting stage of the reaction of dehydrogenation of lower saturated hydrocarbons, while oligomerization of the resulting olefins follows the protonic mechanism; both protonic and aprotic acid sites of the zeolite participate in a subsequent cyclization of oligomers and their unsaturated fragments.

An indiumalumosilicate exhibits a higher acidity compared with the aluminosilicate but yields to the galloalumosilicate in its acidic characteristics.

Thus, the investigation of acidic properties of the catalysts has shown that element-alumosilicates are characterized by different distributions of acid sites in their strength and concentration. The most significant differences are observed in the concentrations of low-temperature acid sites and in the strength of high-temperature acid sites. The differences in the ratio of weak to strong acid sites of element-alumosilicates affect their catalytic properties manifested in the course of propane conversion, since different active centers are responsible for different chemical reactions.

Table 2. Acidic properties of zeolite catalysts.

Catalyst	T _{max} , °C		Concentration, μmol/g		
	T _I	T _{II}	C _I	C _{II}	C _Σ
AS	205	425	676	251	927
Ga-AS	210	450	837	281	1118
In-AS	205	430	795	287	1082

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.

The investigation of the catalytic properties of element-alumosilicates has shown that the catalysts differ from each other in their total (measured by propane conversion degree) and aromatizing reactivities. The data of Table 3 suggest that conversion of propane over aluminosilicate begins at the reaction temperature 400 °C, while the desired products – aromatic hydrocarbons consisting mainly of benzene, toluene and xylenes, are formed at at 500 °C or higher; note that C₉₊ alkylbenzenes, naphthalene and alkylnaphthalenes are also formed in small quantities. The byproducts are represented by gaseous hydrocarbons – methane, ethane and minor amounts of hydrogen and C₂-C₃ olefins.

Table 3. Characteristic of the products of propane conversion over zeolite catalysts.

Catalyst	T, °C	X, %	S ₁ , %	S ₂ , %	S ₃ , %	S ₄ , %	Y _{ArH} , %
AS	400	14	0.4	25.9	5.2	3.6	0.5
	450	30	1.3	55.7	8.5	7.7	2.3
	500	59	2.1	66.4	8.9	17.1	10.1
	550	88	2.5	59.9	7.6	29.1	25.6
	600	99	3.7	60.9	6.0	28.7	28.4
Ga-AS	400	12	4.9	36.9	4.6	12.5	1.5
	450	31	6.6	54.8	5.2	22.9	7.1
	500	70	6.1	49.7	4.1	38.3	26.8
	550	95	5.7	47.0	2.7	43.9	41.7
	600	99	6.3	47.6	2.3	43.3	42.9
In-AS	400	6	0.4	20.6	9.1	3.3	0.2
	450	17	0.9	39.1	13.8	3.5	0.6
	500	37	1.7	60.5	17.8	5.7	2.1
	550	67	2.5	66.0	18.1	10.7	7.2
	600	91	3.3	60.5	14.6	21.3	19.4

Note. X is the propane conversion; S₁, S₂, S₃, and S₄ is the selectivity towards formation of hydrogen, C₁-C₂ alkanes, C₂-C₄ alkenes and aromatic hydrocarbons, respectively; Y_{ArH} is the yield of aromatic hydrocarbons.

The conversion of feedstock and the selectivity towards formation of aromatics increase with increasing process temperature. The conversion and the selectivity towards formation of aromatic hydrocarbons over the AS sample reach 98.5 and 28.8% respectively, at the reaction temperature 600 °C. Thus, the main pathway of conversion of propane over aluminosilicates is its cracking and the selectivity towards formation of arenes is not higher than 30%.

We have found out that an introduction of gallium into the zeolite in the stage of hydrothermal synthesis results in a significant increase in its catalytic reactivity in the course of propane conversion

into aromatic hydrocarbons and its aromatizing activity is exhibited even at a temperature of 450 °C. For the 1.85% Ga-AS sample, the yield of aromatic hydrocarbons at the reaction temperature 600 °C is ~ 43%, which is 1.5 times higher than that for the aluminosilicate at the same reaction temperature. This indicates a promising application of galloalumosilicates as catalysts for aromatization of lower alkanes.

Indiumalumosilicate exhibits the lowest activity in propane aromatization as compared to all the catalysts investigated. An abundant formation of aromatic hydrocarbons was observed only at 550 °C. An increase in the temperature to 600 °C does not result in any significant increase in selectivity towards formation of aromatic hydrocarbons, while the conversion increases to 91%. The reaction products formed in reactions in the presence of this catalyst contain a large number of lower C₂-C₄ olefins.

Figure 2 shows the plots of the selectivity towards formation of aromatic hydrocarbons over element-alumosilicates on the process temperature. It is evident that all samples demonstrate an increased selectivity towards formation of aromatic hydrocarbons with increasing process temperature. The highest aromatizing activity within whole investigated temperature range compared to other catalysts was exhibited by the Ga-AS sample. The monotonic increase in selectivity towards formation of aromatic hydrocarbons with increasing process temperature is characteristic of the In-aluminosilicate. The sharp increase in aromatizing catalytic activity with the process temperature increasing from 450 to 550 °C and the insignificant change in selectivity towards formation of aromatic hydrocarbons during further temperature increase to 600 °C were observed for this aluminosilicate.

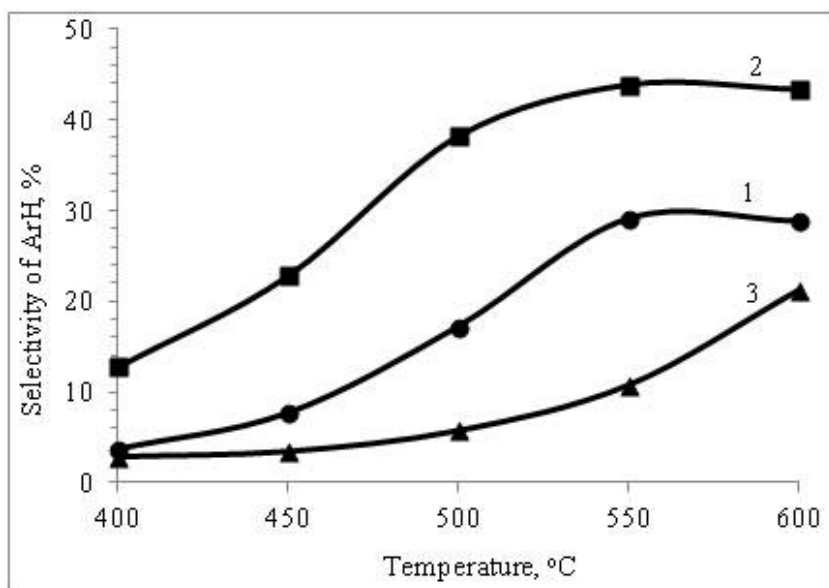


Figure 2. Selectivity towards formation of aromatic hydrocarbons as a function of temperature of propane conversion over the following catalysts: 1 – AS, 2 – Ga-AS; 3 – In-AS.

Thus, an introduction of various modifying additives into the zeolite in the course of hydrothermal synthesis results in samples with different catalytic properties. A zeolite system with an addition of gallium represents the most active and selective catalyst.

The bar chart in Figure 3 shows the effect of the nature of the element introduced into the zeolite on the conversion and yield of aromatic hydrocarbons that are formed on the catalysts at the reaction temperature 600 °C. It is evident that element-alumosilicates exhibit a high catalytic activity in the course of propane conversion but the highest activity is exhibited by the Ga-alumosilicate. A 99%

propane conversion over this catalyst results in a 43% yield of arenes at 600 °C for 500 hr⁻¹. In-AS exhibits the lowest activity during propane conversion and the yield of aromatic hydrocarbons under these process conditions is 19.4%.

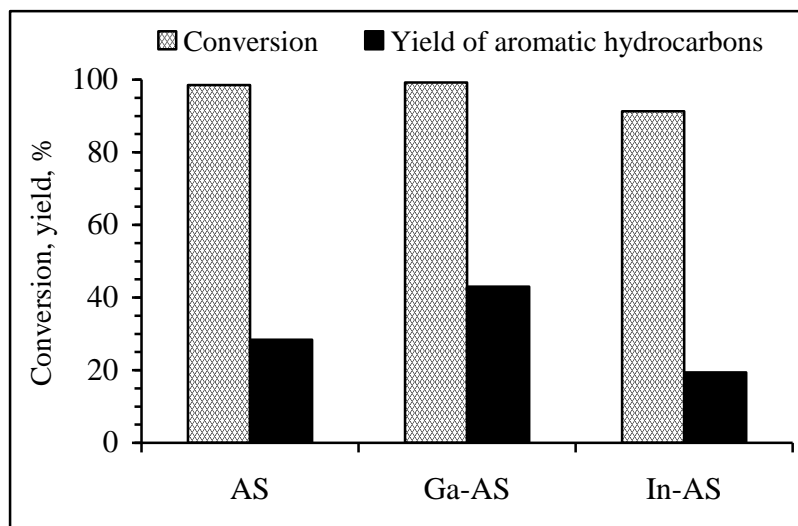


Figure 3. Propane conversion and yield in aromatic hydrocarbons formed over elementoalumosilicate catalysts (T = 600 °C).

4. Conclusion

Thus, we can conclude that an introduction of various modifying additives into the zeolite in the stage of its hydrothermal synthesis results in catalysts that differ in their functional properties. A zeolite, whose crystal lattice contains atoms of gallium along with those of silicon and aluminum, is the most promising for propane aromatization.

5. References

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