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THE PROPERTIES OF ZINC AND GALLIUM CONTAINING PENTASILS – THE CATALYSTS FOR THE AROMATIZATION OF LOWER ALKANES *

V.I. YAKERSON, T.V. VASINA, L.I. LAFER, V.P. SYTNYK, G.L. DYKH, A.V. MOKHOV, O.V. BRAGIN and Kh.M. MINACHEV

N.D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences, Leninsky prospect 47, 117913 Moscow, USSR

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The state of additives (zinc, gallium) in pentasils and their role in the aromatization of ethane and propane have been studied by IR-spectroscopy, analytical electron microscopy and catalytic techniques. The different distribution of additives in the pentasil matrix have been found. Positive effect in aromatization of ethane and propane depends on zinc and gallium content.

The aromatization of lower alkanes over pentasils is of great interest as an additional source of aromatics (Ar) and high octane gasolines. The introduction of zinc and gallium into zeolites enhances overall catalytic activity in hydrocarbon conversion and increases the selectivity to aromatics [1–5].

The present work was undertaken to study the state of the Zn and Ga additives and to explore their role in the aromatization of ethane and propane.

Pentasil catalysts modified with Zn or Ga salts (0.5–5.0% with respect to the metal) were used. The modification was carried out by ion exchange followed by impregnation in the mother solution. The base material was NH_4-pentasil, trade mark ZVM, with the structure of ZSM-5 zeolite ($SiO_2/Al_2O_3 = 30$; 0.04% Na_2O). All samples were heat-treated in air at 300 °C for 2 hours and at 520 °C for 3 hours. The aromatization of lower alkanes (chromatographically pure ethane and propane) was carried out in a flow set-up at atmospheric pressure and a space velocity, LHSV of 120 h^{-1}. The catalyst charge was 2.5 cm^3 (1.7 g) and the duration of each experiment was 4 h. The analysis of gaseous and liquid products was done separately by GC [6].

The nature of the hydroxyl groups was identified and the number of Brönsted (B) and Lewis (L) sites in Zn- and Ga-containing pentasils were evaluated by IR-spectroscopy, using the adsorption of spectral probe molecules–pyridin (Py).

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Table 1
Conversion of ethane and propane over Zn-containing pentasils (600 ° C, LHSV - 120 h^{-1})

Catalyst, composition, %	Conversion, %	Ar yield in % with respect to passed alkane					Gaseous hydrocarbon yield, %			
		Σ Ar	Benzene	Toluene	Xylenes	C_9^+	CH_4	C_2H_4	C_3H_6	C_3H_8
		Ethane								
H-ZVM	20	10	3	4	1	2	8	2	80	–
0.5 Zn/H-ZVM	43	17	6	4	1	6	23	3	57	–
1.0 Zn/H-ZVM	56	25	9	4	1	11	29	2	44	–
2.0 Zn/H-ZVM	83	17	5	4	1	7	65	1	17	–
3.0 Zn/H-ZVM	90	17	4	5	1	7	72	10	10	–
5.0 Zn/H-ZVM	89	15	2	2	–	11	73	1	11	–
		Propane								
H-ZVM	98	37	14	10	21	11	41	1	19	2
0.5 Zn/H-ZVM	99	51	18	13	3	17	25	2	21	1
1.0 Zn/H-ZVM	99	46	17	11	2	16	26	1	26	1
2.0 Zn/H-ZVM	100	41	11	9	2	19	40	1	18	–
3.0 Zn/H-ZVM	100	44	12	11	2	19	40	2	14	–
5.0 Zn/H-ZVM	100	48	15	14	4	15	41	1	10	–

The experiments were done in a quartz vacuum cell, connected with an adsorption set-up. IR-spectra were recorded with a "Specord M80" instrument according to the technique described in [7]. To characterize the zinc and gallium components an analytical electron microscope EM-100C, equipped with a goniometer and an energy dispersive X-ray analysis unit KEVEX-5100 was used. Thus, from the same particle of the catalyst sample, its image, electron diffraction pattern and energy dispersive spectrum of characteristic X-ray emission could be registered.

The introduction of relatively small amounts (0.5–1%) of these additives appreciably enhances the yields over the pentasil zeolite in ethane and propane conversion. Thus the reaction of propane over nonmodified zeolite gives 37–39% of Ar and 40% of CH_4, while the introduction of only 0.5% Zn increases the Ar yield up to 52% and decreases the CH_4 formation down to 17–25%. A much more pronounced effect was observed for ethane. In this case the conversion on addition of Zn continuously increases from 20 up to 90% and the yield of Ar on addition of 0.5–1% Zn increases by 2–2.5 times (see table 1).

The introduction of gallium into pentasil (0.5–2%) also accelerates aromatization of ethane and propane compared to the original H-ZVM. Ar yield increases by a factor of three reaching 60% in the presence of 2% gallium. Further increase of the gallium up to 3% leads to considerable decrease of aromatizing properties of the catalyst (see fig. 1). At the same time H-pentasils not containing zinc and gallium ions also possess appreciable activity in aromatization. Taking this into

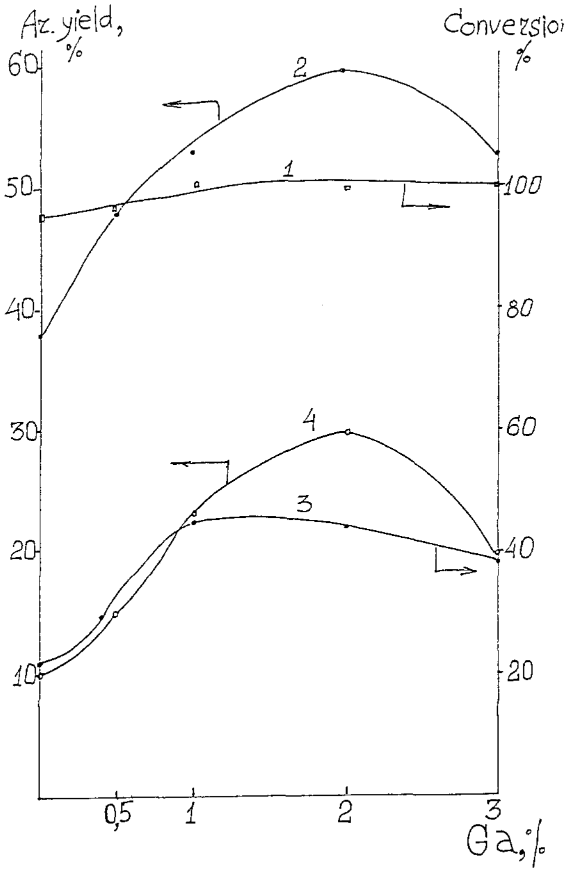

Fig. 1. The effect of Ga concentration in pentasil H-ZVM on the catalytic properties in propane (1,2) and ethane (3,4) conversion; 1,,3-conversion, 2,4-overall Ar yield ($T = 600\,^{\circ}\mathrm{C}$, LHSV = 120 h^{-1}).

account it may be assumed that, in this case, aromatization proceeds by another path-way, in which the protons of OH-groups act as acceptors of hydride ions. This is probably the reason why H-pentasils are less active [3–5].

To elucidate the state and functions of additives (Zn and Ga) we studied the nature of the hydroxyl groups, acidic properties and distribution of Zn and Ga ions in the channels and on the surface of pentasil (IR-spectroscopy, electron microscopy).

According to the data on the adsorption of Py, the initial H-form of ZVM contains three types of acidic sites: (i) strong B_I-sites amounting to 575 ± 25 μmol/g being characterized by an OH absorption band (a.b.) at 3610 cm^{-1}, (ii) less strong B_{II}-sites (of 200 μmol/g); in this case the proton in the OH-group is strongly delocalized and (iii) L-sites which amount to 140 μmol/g. Introduction of Zn^{2+} leads to decrease of overall B-sites number down to about 200 μmol/g

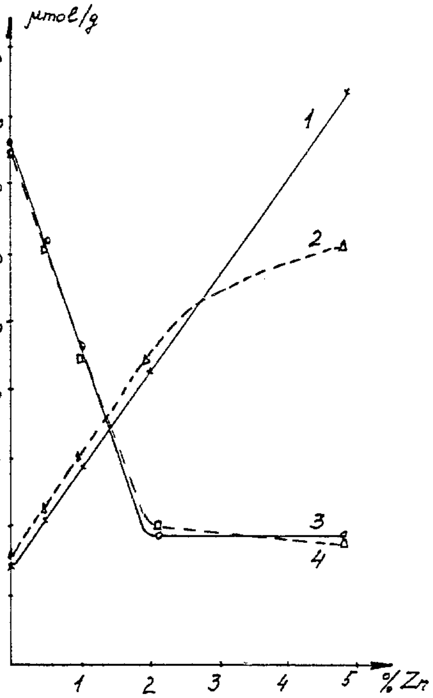

Fig. 2. The dependence of the number of B- and L-sites on Zn concentration in Zn/H-ZVM system; 1,2-L-sites; 3,4-B-sites; 1,3-calculated; 2,4-experimental.

for 1.5–5% of zinc. This value is in accordance with the number of B_{II}-sites. The number of L-sites linearly increases upon introduction of zinc and at zinc concentration of 2–5% deviation from this linearity is observed. The decrease of B-sites number on introduction of zinc results from proton exchange of the most acidic OH-groups for Zn^{2+} ions, which are the source of additional L-sites.

We may therefore calculate the number of B- and L-sites in Zn- and Ga-containing zeolites. Thus, if in the initial H-ZVM sample the number of L-sites is 140 μmol/g and the number of B_I-sites, which are capable to exchange is equal to 575 μmol/g, then introduction of, for example, 0.5% Zn^{2+} (corresponding to 76 μmol/g) should increase the number of B_I-sites by 2×76 μmol/g, since each Zn^{2+} ion substitutes 2 protons of an OH-group. Therefore, in case when 0.5% Zn^{2+} is added the sample will contain $140 + 76 = 216$ μmol/g of L-sites and $575 - 152 = 423$ μmol/g of B_I-sites, while the number of B_{II}-sites will remain constant. Plots presented in fig. 2 show the dependence of the number of B- and L-sites in the Zn/H-ZVM catalyst upon the Zn content. Close agreement of experimental and calculated results shows the authenticity of the proposed mechanism for H-ZVM modification by zinc. The deviation of the experimental curve from the calculated one for the number of L-sites reflects transformation of ion exchangeable form of Zn^{2+} to the form in which part of ions Zn^{2+} are not accessible for Py adsorption. Thus, on modification of the zeolite by zinc the Zn^{2+} ions exchange with protons of strongly acidic OH-group, less strong B_{II}-sites not taking a part in the exchange. Zn^{2+} ions, which substitute the protons in OH-groups, are the source of additional acidity (L_{II}) together with L_I-sites already present in the zeolite. At higher Zn content ($>2\%$) the third type of L_{III}-sites appears. These are excess Zn^{2+} ions, which do not undergo the exchange process.

In the Ga^{3+}/H-ZVM system the concentration of B_I-sites, which can be characterized by a.b. at 3610 cm^{-1}, is only feebly dependent on Ga content in the range 0.5–5% and amounts to 575 ± 25 μmol/g. The number of L-sites slightly increases with Ga concentration and this increase of Ga content leads to appearance of a second type of sites, L_{II}, which are absent in the initial zeolite. Thus, in the Ga^{3+}/H-ZVM system there are L_I-sites with constant concentration and L_{II}-sites their number increasing with Ga content almost linearly. However, the increase of the number of L_{II}-sites is insignificant. This shows that most of the Ga does not interact with Py as L-sites. It can be also concluded that there are two types of B-sites in the catalyst: (i) more strong sites, B_I, which are characterized by a.b. at 3610 cm^{-1} and concentration of 575 μmol/g and (ii) less strong ones, B_{II}, which do not exhibit any clear a.b. of the OH-group but can be detected by thermal desorption of Py. The concentration of B_{II}-sites amounts to about 200 μmol/g, i.e. about 3 times as low for this particular pentasil sample. The Ga does not interact with OH-groups and the behaviour and the concentration of the latter do not depend on the presence of Ga. Unlike Zn, Ga ions, probably, do not occupy cation positions and are not located in zeolite channels. Most probably they are located on the external surface of the zeolite in aggregated form as gallium oxide. This agrees with the only small increase of the number of L_{II}-sites with Ga content that can be explained by the formation of rather large Ga_2O_3 crystals on the outer surface of the zeolite. The only Ga^{3+} ions which are located on the external surface are responsible for the formation of L_{II}-sites. At the same time there are also "the old" L_I-sites which belong to initial zeolite and their concentration does not depend on Ga content.

Additional experimental evidences for above-mentioned assumptions concerning the distribution of Zn^{2+} and Ga^{3+} ions in pentasil matrix were found by carrying out an electron microscopy study of pentasils containing 5% of Zn or 2% Ga. In case of the Ga^{3+}/H-ZVM system Ga was not detected in pseudohexagonal plates which are characteristic for zeolite (fig. 3). Ga can be seen only as an individual morphological formation located on the outer surface of zeolite which are extended microcrystals sized in the range $0.2\text{–}0.25 \times 0.05$ μ. As it was established by the electron microprobe method Zn is always present in pseudohexagonal plates of Zn^{2+}/H-ZVM zeolite. The content of Zn in respect to other elements (Si, Al) in all particles is nearly constant (fig. 4). Thus the distributions of activators–Zn and Ga–upon their introduction into zeolites are different. Ga does not penetrate into the channels of zeolites and is located as an individual

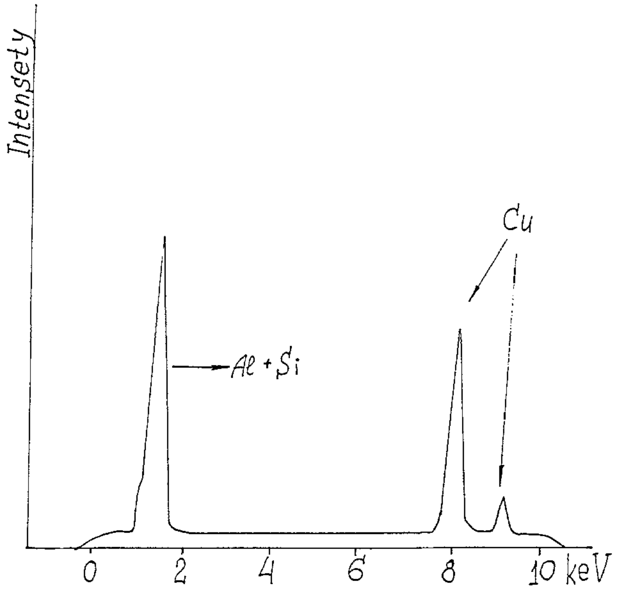

Fig. 3. Energy dispersive spectrum of characteristic X-ray emission for the plate of Ga-containing zeolite (Al and Si lines correspond to zeolite framework, Cu - to copper grid of holders, Ga lines are absent).

oxide phase on the outer surface of the catalyst, whereas Zn tends to distribute itself uniformly in the zeolite channels.

Considering all these data we note two important features. The first is the positive effect of introducing Zn and Ga into zeolites; this leads to considerable

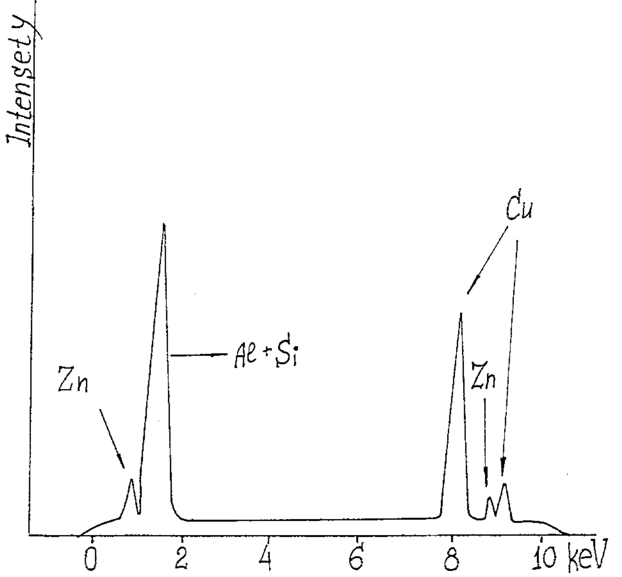

Fig. 4. Energy dispersive spectrum of characteristic X-ray emission for plate of Zn-containing zeolite (for Al, Si and Cu lines see fig. 3; Zn lines belong to zinc in zeolite matrix).

increase of the rates of lower alkanes aromatization. The second is the different distribution of the two additives in the pentasil matrix. This difference in distribution may be caused by the fact that the last additive is a multicharged ion and therefore in order to compensate the charge the Ga ions should be distributed in the zeolite structure as aquacomplexes and bridged structures [8]. The distribution of such structures in zeolite channels is hindered because of steric reasons. At the same time, in spite of the different distribution of Ga compared to Zn the introduction of Ga also shows a positive effect in aromatization and this effect depends on gallium content. There are several reasons for this effect: (i) it is possible that the reaction media or pretreatment in different gases that have strong influence on catalytic properties [9] may cause dispersity of the Ga-containing phase and migration of the dehydroxylated Ga ions into the zeolite channels; (ii) it can not be ruled out also that activation of alkane molecules proceeds directly on the surface of Ga-containing phase followed by conversion of intermediates in zeolite channels. These reasons merit further study.

References

[1] M. Shibata, H. Kitagawa, Y. Sendola and Y. Ono, 7th Int. Conf. Zeolite Catalysis, Tokyo 1986, 717.

[2] G. Sirokman, Y. Sendola and Y. Ono, Zeolites 6 (1980) 299.

[3] T. Mole, J.R. Anderson and G. Greer, Applied Catalysis 17 (1985) 141.

[4] O.V. Bragin, T.V. Vasina, S.A. Isaev, G.A. Kudryavtseva, V.P. Sytnyk and A.V. Preobrazhensky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 37 (1988) PI 24.

[5] N.S. Gnep, J.Y. Dojemet, A.M. Seco, F.R. Ribeiro and M. Guisnet, Applied Catalysis 43 (1988) 155.

[6] O.V. Bragin, A.V. Preobrazhensky and A.L. Liberman, Izvestiya academii Nauk SSSR, Seriya Khimicheskaya (1974) 275 (Russ).

[7] L.I. Lafer, G.L. Dykch, V.I. Yakerson, V.P. Sytnyk, T.V. Vasina and O.V. Bragin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 38 (1989) No. 3.

[8] D.W. Breck, *Zeolite Molecular Sieves* (Wiley-Interscience, 1974).

[9] Y. Shibin, S. Liqin, L. Xingyun and L. Xuanwen, Proc. 3th China-Japan-US Symp. in Catalysis, China B-63 (1987) p. 91.