The effect of the nature of a modifying additive (Pt, Zn, Ga) on the activity of oxide and zeolite catalysts in ethane dehydrogenation and aromatization

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The catalytic properties of Pt, Zn, and Ga deposited on supports of various natures $(Al_2O_3, SiO_2, NaZSM, and HZSM)$ in the dehydrogenation and aromatization of ethane were investigated. Pt-containing catalysts are the most active in the conversion of ethane: the selectivity with respect to ethylene is 25–87 % depending on the nature of the support. In the presence of Zn- and Ga-containing catalysts the yield of ethylene is 2–3 times lower than with Pt-catalysts. With HZSM modified by Pt, Zn, or Ga aromatic hydrocarbons (ArH) and methane are the main products of ethane transformation. Ga/HZSM is the most efficient catalyst of the aromatization of ethane under the conditions studied (550 °C, 120 h⁻¹).

Key words: catalysis, dehydrogenation, aromatization, ethane, ethylene, modified oxides and pentasils.

Modification of pentasils with Group VIII metals or Zn, Ga, and Cr cations is known to increase their activity in the aromatization of lower alkanes.¹⁻⁵ As a rule, this is assumed to be due to the activity of the additives introduced in the dehydrogenation of alkanes, since the olefin formation step is considered the limiting step in the aromatization process. While in the aromatization of $C_3 - C_5$ alkanes, cracking of the starting hydrocarbons may be an alternative source of olefins,^{5,6} in the case of ethane, dehydrogenation of the starting alkane followed by oligomerization, cracking, and aromatization is the only pathway for the formation of aromatic products. Therefore, using ethane as an example one can follow most accurately the relationship between the activity of a modifying agent in dehydrogenation on applied catalysts and the activity of the modified pentasil in aromatization.

In the present work we studied the catalytic properties of platinum, zinc, and gallium deposited on supports of various natures $(Al_2O_3, SiO_2, NaZSM, and HZSM)$ in the dehydrogenation and aromatization of ethane.

Experimental

Modified catalysts were prepared according to the known procedure⁷ by impregnating Al_2O_3 , SiO_2 , NaZSM, and HZSM with aqueous solutions of the corresponding Pt, Zn, and Ga compounds. The content of the modifying agents in the resulting catalysts was 0.5 % w/w of Pt and 2.0 % w/w of Zn or Ga. Aluminum oxide was prepared by calcination of aluminum

hydroxide at 520 °C for 6 h; SiO₂ was obtained from silicic acid (SiO₂ · nH_2O). The Na-form of the ZSM-type zeolite (SiO₂/Al₂O₃ = 42) whose synthesis and properties have been reported,⁸ was preliminarily calcined in a dry air flow for 5 h at 550 °C. The H-form of the zeolite was prepared from NaZSM by three-stage ion exchange of Na⁺ with NH₄⁺ with the subsequent decomposition of NH₄ZSM at 550 °C for 5 h.

Prior to the experiments all of the catalyst specimens were calcined in a dry air flow (520 °C, 5 h); Pt/HZSM and Ga/HZSM were calcined either in an air flow or in an air flow and then in a H_2 flow (520 °C, 2 h).

The experiments were carried out in a flow-type unit at temperatures of 550–700 °C and a volumetric ethane rate (v) of 120–1200 h⁻¹. The reaction products were analyzed by GLC. The main results are presented in Tables 1 and 2 and in Figs. 1 and 2.

Results and Duscussion

To estimate the contribution of thermal processes we carried out experiments on quartz and Zn- and Ga/NaZSM at temperatures of 550-700 °C and $v = 120 h^{-1}$. At 550 °C, the degree of ethane conversion (x) on quartz is only 0.3 %. As the temperature increases to 600 °C, x increases by an order of magnitude, and at 650-700 °C x is as high as 20-42 %. The major product of the transformation of ethane at temperatures below 650 °C is ethylene; at higher temperatures methane forms. It should be noted that over the temperature range studied the effect of zinc and gallium oxides on the conversion of ethane is insignificant.

The data presented in Table 1 indicate that under the conditions studied (550 °C, 120 h⁻¹) unmodified Al₂O₃,

Catalyst	x (%)	Yield of products (% w/w)		
		CH ₄	C ₂ H ₄	
SiO ₂	0.5	-	0.5	
Al ₂ O ₃	0.4	-	0.4	
NaZŚM	0.9	traces	0.9	
Pt/SiO ₂	8.0	1	7.0	
Pt/Al203*	24.0	16	6.0	
Pt/NaZSM	9.0	2	7.0	
Ga/SiO ₂	3.0	traces	3.0	
$Ga/Al_2\tilde{O}_3$	7.0	1	6.0	
Ga/NaZSM	1.5	traces	1.5	
Zn/SiO_2	2.0	traces	2.0	
$Zn/Al_2\tilde{O}_3$	4.0	traces	4.0	
Zn/NaZŠM	2.0	traces	2.0	

Table 1. Transformation of ethane on modified catalysts (550 °C, 120 h^{-1})

* The yield of $C_3 - C_4$ hydrocarbons amounts to ~2 % w/w.

 SiO_2 , and NaZSM do not exhibit noticeable catalytic activity: the degree of ethane conversion is as low as 0.4-0.9 %.

Modification of the various support materials with Pt affects x and the yield of ethane in different ways. For example, in the presence of Pt/SiO_2 and Pt/NaZSM, x = 7.5-9.0 %; the main reaction product is ethylene. In the case of $Pt/Al_2O_3 x$ is much higher and may be as high as 24 %, mostly due to an increase in the cracking. The yield of methane from this specimen is 2.5-fold higher than that of ethylene. In addition, a certain amount of C_3-C_4 hydrocarbons forms.

Table 2. Aromatization of ethane on modified pentasils (550 °C, 120 h^{-1})

Catalyst	x (%)	Yield (% w/w)			S (%)	
		CH ₄	C_2H_4	ArH	ArH	CH ₄
HZSM	3.5	2.5	1	traces		
Ga/HZSM	23.0	6.0	2	15	65	26
Pt/HZSM	50.0	31.0	4	15	30	62
Zn/HZSM	54.0	36.0	2	16	30	67

Of the Ga-containing catalysts, Ga/Al_2O_3 is the most active in the dehydrogenation of ethane: the yield of ethylene with this catalyst is comparable with that for Pt/Al_2O_3. The Ga/SiO_2 catalytic system possesses lower dehydrogenating ability than Ga/Al_2O_3, and the Ga/NaZSM specimen is practically inactive in this reaction (see Table 1). When Ga ions are deposited onto the silica or, especially, alumina surface, the sites necessary for polarization of the C—H bonds in ethane and for dehydrogenation to occur are probably formed. In fact, it was shown^{9,10} that applying gallium ions onto silica gel and alumosilicate results in the formation of both proton-donating and electron-withdrawing sites (Ga³⁺) in which activation of ethane molecules may occur.

It was shown¹¹ that dehydrogenation of propane in the presence of Ga/HZSM-5 is faster than with Ga/NaZSM-5, since in the presence of a proton the slow olefin formation step is no longer the limiting step of the process.



Fig. 1. Time variation of the degree of ethane conversion (a) and yield of ethylene (b) at 550 °C and $v = 120 \text{ h}^{-1}$ in the presence of: Pt/Al₂O₃ (I), Pt/NaZSM (2), Pt/SiO₂ (3), Ga/Al₂O₃ (4), Zn/Al₂O₃ (5).



Fig. 2. The dependence of the degree of ethane conversion (1, 2), and yields of ArH (3, 4) and ethylene (5, 6) on the volumetric rate in the presence of modified pentasils Pt/HZSM (1, 3, 5) and Ga/HZSM (2, 4, 6) at 550 °C.

The results obtained by us on dehydrogenation of ethane with Ga/Al_2O_3 , Ga/SiO_2 , and Ga/NaZSM agree well with the results obtained in Refs. 11 and 12. All of the foregoing indicates that when support materials are modified with gallium, the presence of acidic OH groups is necessary for the formation of active sites.

Zn-containing catalysts possess lower activities than Pt- and Ga-specimens. Of these, Zn/Al_2O_3 is the most active.

Based on the data obtained the catalysts under study may be arranged in the following order according to their activity in the formation of ethylene:

 $\begin{array}{l} {\rm Pt}/{\rm Al}_2{\rm O}_3 \sim {\rm Pt}/{\rm SiO}_2 \sim {\rm Pt}/{\rm NaZSM} \\ {\rm Ga}/{\rm Al}_2{\rm O}_3 > {\rm Ga}/{\rm SiO}_2 > {\rm Ga}/{\rm NaZSM} \\ {\rm Zn}/{\rm Al}_2{\rm O}_3 > {\rm Zn}/{\rm SiO}_2 \sim {\rm Zn}/{\rm NaZSM} \end{array}$

Figure 1 presents the variation of the degree of ethane conversion (x) and the yield of ethylene in the course of the dehydrogenation of ethane on Pt-, Zn-, and Ga-containing catalysts based on Al₂O₃, SiO₂, and NaZSM. It can be seen that the Pt-containing specimens differ substantially from the Zn- and Ga-containing contacts. The x values, which are relatively high at the beginning of the process for all of the Pt-containing catalysts, decrease within two hours by a factor of 2-3,

due most of all to decreases in the cracking process and in the yield of methane. The variation of the yield of ethylene depends substantially on the nature of the supporting material: in the case of Pt/Al_2O_3 the catalytic activity with respect to dehydrogenation of ethylene increases, due to the development of the catalyst, as was shown before in the study of aromatization of lower alkanes and alkenes.¹³ In the presence of Pt/SiO_2 the yield of ethylene decreases somewhat with time, and on Pt/NaZSM it practically does not change.

For Ga- and Zn-containing catalysts based on SiO_2 and NaZSM, the x values and yields of ethylene are commensurable (see Table 1) and do not change with time; with catalysts based on Al_2O_3 , x is higher than the yield of ethylene (see Fig. 1).

The results of the transformation of ethane in the presence of HZSM and its modified forms (550 °C, 120 h⁻¹) are summarized in Table 2. In the presence of HVZM under the conditions studied x does not exceed 4 % and methane and ethylene are the prevailing products.

When the modifying additives (Pt, Zn, Ga) are introduced into HVZM, the x value drastically increases, and is as high as 23 % with Ga/HZSM, 50 % with Pt/HZSM, and 54 % with Zn/HZSM. The main reaction products are ArH and methane.

Of the catalysts investigated, Ga/HZSM is the most efficient in the aromatization of ethane under the conditions studied: the yield of ArH with this catalyst is 15 % and the selectivity (S_{ArH}) is 65 %. The yield of ArH with Pt- and Zn-containing pentasils is comparable to that in the presence of Ga/HZSM, however, S_{ArH} is half as high. The degree of ethane conversion decreases in the following order:

Zn/HZSM > Pt/HZSM > Ga/HZSM

and S_{ArH} changes in the reverse sequence:

Ga/HZSM >> Pt/HZSM = Zn/HZSM

The relatively low S_{ArH} in the case of Pt- and Zn/HZSM (30 %) is due to intense cracking and the formation of substantial amounts of methane (see Table 2).

Figure 2 presents the dependence of the degree of ethane conversion and the yields of ArH and ethylene on the volumetric rate with Pt- and Ga/HZSM catalysts (the specimens were treated with air and H_2). As was shown above, the contribution of Pt to the dehydrogenation of ethane is higher than that of Ga (see Table 1), however, the yields of ArH under the conditions of the aromatization of ethane on Pt- and Ga/HZSM are commensurable. As the volumetric rate increases, the degree of conversion and the yield of ArH decrease and the yield of ethylene changes insignificantly.

In general, the data obtained imply that the contributions of the modifying agent and the support to the processes of dehydrogenation and aromatization of ethane cannot be considered separately. Acidic properties of the support (the number and strength of acidic sites) in combination with the distribution of the modifying additives and their interaction with the support determine the activity of a catalytic system at various stages of the complex multistage aromatization process.

References

- 1. T. Mole, J. R. Anderson, G. Greer, Appl. Catal., 1985, 17, 141.
- 2. N. S. Gnep, J. Y. Doyemet, A. M. Seco, F. R. Ribeiro, and M. Guisnet, *Appl. Catal.*, 1988, **43**, 155.
- Kh. M. Minachev and A. A. Dergachev, Usp. Khim., 1990, 59, 1522 [Russ. Chem. Rev., 1990, 59 (Engl. Transl.)].
- 4. T. Inui, Stud. Surf. Sci. Catal., Elsevier, Amsterdam, 1989, 44, 189.
- O. V. Bragin, T. V. Vasina, V. P. Sitnik, N. V. Nekrasov, and V. I. Yakerson, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1250 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, 39, 1121 (Engl. Transl.)].

- cessful Design of Catalysis, Elsevier, Amsterdam, 1989, 44, 279.
- 7. S. Engels, H. Lausch, B. Matschel, O. V. Bragin, and A. V. Preobrazhensky, *Catal. Today*, 1988, **3**, 437.
- 8. V. Yu. Volkov, M. A. Kaliko, B. A. Lipkind, and V. V. Zadymov, *Khim. i Tekhnol. Topliv i Masel* [*Chem. and Technol. of Fuels and Oils*], 1982, **6**, 8 (in Russian).
- A. D. Motina, E. V. Smekalina, A. D. Razumaeva, A. L. Il'inskii, and E. V. Lunina, *Zh. Fiz. Khim.*, 1989, 63, 2679 [*Rus. J. Phys. Chem.*, 1989, 63 (Engl. Transl).
- E. V. Lunina, A. D. Motina, and G. L. Markaryan, *Zh. Fiz. Khim.*, 1990, **64**, 2730 [*Rus. J. Phys. Chem.*, 1990, **64** (Engl. Transl).
- 11. P. Meriaudeau and C. Naccache, J. Mol. Catal., 1990, 59, 31.
- V. B. Kazansky, L. M. Kustov, and A. Yu. Khodakov, Stud. Surf. Sci. Catal., Elsevier, Amsterdam, 1989, 49, 1173.
- O. V. Bragin, E. S. Shpiro, A. V. Preobrazhenskii, T. V. Vasina, G. V. Antoshin, and Kh. M. Minachev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1256 [Bull. Acad. Sci. USSR, Div. Chem. Sci., 1980, 29, 880 (Engl. Transl.)].

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