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**ON THE INCORPORATION OF GALLIUM IONS  
INTO A CATIONIC SITES OF PENTASIL RING  
ZEOLITES AND THEIR ACID-BASE, REDOX  
AND CATALYTIC PROPERTIES**

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*Ga-zeolites of MFI and BEA topology were prepared by three different methods: conventional ion exchange of gallium ions from solution of gallium salt, reductive solid state reaction of gallium oxide with H-form of zeolite, and interaction of GaCl<sub>3</sub> with H-form of zeolite. They were characterized by XRD, XRF, H<sub>2</sub>-TPR, FTIR, the adsorption of pyridine and d<sub>3</sub>-acetonitrile. The catalytic activity of Ga-zeolites was studied in plug-flow reactor in a steady state at atmospheric pressure. XRD and TPR evidence shows the presence of at least three kinds of species: a) (GaO)<sup>+</sup> in the cationic sites; b) gallium is in the form of bulk oxide; c) Ga<sup>3+</sup> ions. The number of Lewis sites increases as the Brønsted sites decrease upon introduction of Ga ion. (GaO)<sup>+</sup> ions are the easiest reducible and exhibit the highest catalytic activity in ammoxidation of propane to acrylonitrile.*

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## Introduction

The increasing volume of chemical production, insufficient availability and high prices of the olefins stimulate and increase interest in the innovation of current processes. Substitution of olefins by much cheaper and more abundant alkanes belongs to one of the main trends in innovating chemical processes. However, a direct conversion of alkanes to more valuable chemicals faces the problem of their high chemical stability compared to olefins. The second possibility is to use two-step process, where in the first step alkanes are converted into olefins via oxidative dehydrogenation, followed by selective oxidation or ammoxidation to demanded products. These processes usually take place over mixed metal oxides. Although such a process for propane is in pilot plant stage, realization of the two-step process is breaking down due to the problems with heat removal, problems with preventing complete oxidation of olefins to carbon oxides, as well as with high cost of the dehydrogenation unit. Therefore, a great effort is made to search for selective catalysts for direct conversion of alkanes into valuable products.

Acrylonitrile is a major chemical commodity used in a variety of applications [1], mainly as a raw material in the manufacture of polyacrylonitrile fibers, plastics, adiponitrile, acrylamide and nitrile rubber. More than 4.5 millions tons of acrylonitrile (90 % of all production [2]) are produced worldwide by SOHIO Corp. which invented a process based on ammoxidation of propene at 650 K over mixed oxide U-Sb-O or Mo-Bi-O [3,4].

Direct catalytic ammoxidation of propane to acrylonitrile can be carried out on oxide catalysts based on V-Sb [5,6], V-Bi [7–9], V-Ga and Sb-Ga [10–12] or V-Mo [14,15]. However, the reaction requires a high reaction temperature ~ 800 K, i. e. about 100 – 150 K higher than that for propene ammoxidation. The highest yields of acrylonitrile (35 % yield at 60 % conversion) are achieved on a metal oxide catalyst based on V-Sb-Al-O [13]. However, such parameters are not sufficient for commercial application. This is the reason why the attention in the field of activation and conversion of paraffins to oxygenates turns to other catalytic systems like zeolites bearing atomically dispersed metal ions.

In 1997 Armor *et al.* [16–18] reported direct selective ammoxidation of ethane to acetonitrile over Co loaded high silica zeolites with MFI, BEA and NU-1 topologies. The yield of acetonitrile was reported to reach 26 %, while the best oxidic systems V-P-O, Nb-Sb-O and Cr-Nb-Mo-O oxides attained only several per cents in the same conditions.

Our studies of ethane and propane oxidative dehydrogenation and ammoxidation on Co-zeolites of MFI, BEA, FER and MOR topologies [19,20] revealed that the highest activity of Co ions in both reactions was found with Co-BEA and Co-MFI zeolites, while Co ions in MOR and FER exhibited very low activity. The results indicate that some shape selective effect regarding the level of accessibility of reaction intermediates is likely to play role in oxidation and

ammoxidation of paraffins over Co-zeolites. In addition, it has been found that ammoxidation of propane leads with high selectivity exclusively to formation of propene and acetonitrile, not to acrylonitrile. Formation of acetonitrile proceeds either during the addition of ammonia to propylene, or if acrylonitrile is formed, it is readily decomposed over Co ions to acetonitrile and some hydrocarbon rest, which is immediately oxidized to carbon dioxide.

In 2001 Derouane-Abd Hamid *et al.* [21,22] reported catalytic activity of Ga-modified MFI zeolites prepared by ion-exchange of gallium from gallium nitrate solution in direct ammoxidation of propane to acrylonitrile. The catalysts exhibited acrylonitrile yield about 50 % of those of conventional V-Sb-O mixed oxides. But this catalytic system shows two major advantages: a very low yield of carbon oxides and surprisingly high selectivity to C<sub>4</sub> hydrocarbons, in particular isobutane and isobutene [22]. The suggested reaction mechanism of propane ammoxidation over Ga-MFI zeolites assumes that Brønsted acid sites play a role in synergy with Ga species. However, detailed studies are missing about the structure and function of active sites and analysis of the effect of topology and composition of zeolite matrix on catalytic activity of Ga-zeolites.

Incorporation of gallium can be achieved by ion exchange from aqueous solution [23,24], impregnation [25] and solid-state ion exchange in physical mixtures with Ga<sub>2</sub>O<sub>3</sub> [26] or GaCl<sub>3</sub> [27] at high temperatures. Gnep [28] and Kitagawa [23] observed that their preparation method did not result in a significant decrease in acidity of the gallium containing MFI zeolite. Similar results have been published by Anunziata [29], who assumed that the gallium after ion exchange is mainly located at the external surface.

There is evidence that at elevated temperature and under reducing conditions Ga<sup>+</sup> ions are able to enter the zeolite channels. This process is probably initiated by reduction of Ga<sub>2</sub>O<sub>3</sub> by H<sub>2</sub>, followed by ion migration possibly as Ga<sub>2</sub>O vapour [24,26]. Heating of physical mixtures of GaCl<sub>3</sub> and dehydrated zeolite (CVD method) is more efficient to position Ga into zeolite cavities than ion exchange from an aqueous solution of a Ga<sup>3+</sup> salt [27]. It appears that the position of gallium depends strongly on the activation treatment and the method of preparation.

In this paper, we report on a study of the nature and catalytic activity of the gallium ions after introduction into zeolite by different methods and on the acidity induced by them. For this purpose, we combined FTIR spectroscopy of adsorbed pyridine and d<sub>3</sub>-acetonitrile, temperature-programmed reduction (H<sub>2</sub>-TPR), N<sub>2</sub> adsorption and catalytic test. The aim is to design preparation methods yielding a high level of ion exchange for the synthesis of catalysts active in the ammoxidation of propane.

## Experimental

### Preparation of Catalysts

The incorporation of gallium into high silica pentasil ring zeolites and the catalytic activities of these materials in ammoxidation of propane were studied on a set of materials prepared by three different methods: by conventional ion exchange of gallium ions from solution of gallium salt, reductive solid state reaction of gallium oxide with H-zeolite and interaction of  $\text{GaCl}_3$  with H-zeolite.

#### *Ga-MFI-IE*

H-MFI zeolite with Si/Al = 14 was obtained from Institute of Oil and Hydrocarbon Gases, Slovnaft, Slovakia. Ga-modified zeolites were obtained by ion exchange of 4 g of H-MFI with gallium nitrate solution (0.05 M). The mixture was stirred for 75 min at 45 °C and then for 4 h at 100 °C under reflux. The solid was collected by filtration, washed and dried overnight at 25 °C. The material was then calcined at 150 °C for 2 h, heated further to 450 °C in a stream of helium.

#### *Ga-BEA-CVD*

The Ga-BEA-CVD sample was prepared by chemical vapor deposition (CVD), i.e., subliming  $\text{GaCl}_3$  into H-BEA with Si/Al = 9.5 obtained from Research Institute of Inorganic Chemistry, Inc., Unipetrol, Ústí n. L. The volatility of  $\text{GaCl}_3$ , in combination with its low boiling point (201 °C), makes this chloride into a suitable candidate for direct sublimation into the cavities of dehydrated H-BEA zeolite. A 1.45 g H-BEA zeolite sample was calcinated with excess of  $\text{GaCl}_3$  under nitrogen at a flow rate of 100 ml min<sup>-1</sup>. The temperature was increased from RT to 700 °C at a rate of 8 °C min<sup>-1</sup> and then held at 700 °C for 4 h. After CVD the sample was hydrolyzed twice with 120 ml of water at 40 °C for 4 h in order to remove unreacted chloride.

#### *Ga-BEA-SSR*

2 g H-BEA zeolite with Si/Al = 12.7 synthesized at Heyrovský Institute of Physical Chemistry, Academy of Sciences of Czech Republic, was physically mixed with 0.415 g gallium oxide in a mortar with pestle. The mixture was loaded into ball-mill and ground for 3 h. The solid was heated in reduction gas mixture (70 vol. % nitrogen and 30 vol. % hydrogen) at a rate of 8 °C min<sup>-1</sup> to 700 °C and kept at this temperature for 8 h.

## Characterization of Catalysts

Composition of the catalysts was determined in pellets of zeolite with boric acid by means of wavelength-dispersed X-ray fluorescence spectrometer Spectroscan U (Spectron Optel, St. Petersburg, Russia). The experimental conditions of analysis were described elsewhere [30].

Nitrogen adsorption isotherms were measured at liquid-nitrogen temperature ( $-196\text{ }^{\circ}\text{C}$ ) on a self-constructed chromatographic apparatus by thermal desorption method [31] and the specific surface area was determined by means of BET isotherm equation [32]. Before the experiment, the sample (about 50 mg) was dehydrated at  $350\text{ }^{\circ}\text{C}$  for 2 h in a stream of helium ( $25\text{ ml min}^{-1}$ ).

Crystallinity and X-ray powder diffraction (XRD) patterns of the Ga-zeolites were investigated with a Bruker D8 Advance diffractometer using Cu  $K\alpha$  radiation.

For FTIR analysis, samples were pressed into self-supported wafers. Spectra were recorded between  $4000 - 600\text{ cm}^{-1}$  on a Nicolet Protege 460 FTIR spectrometer equipped with an MCT detector. The wafers ( $\sim 10\text{ mg cm}^{-2}$ ) were heated up to  $450\text{ }^{\circ}\text{C}$  under reduced pressure (0.5 Pa) for 3 h and then the IR spectra were recorded at RT. The adsorption of the probe molecules (pyridine and  $d_3$ -acetonitrile) was measured too. The probe molecule vapour was introduced into the cell at RT (0.5 kPa), and then desorption was performed under reduced pressure (0.5 Pa) for 15 min at the following temperatures: RT, 100, 200, 300 and  $450\text{ }^{\circ}\text{C}$ .

Temperature-programmed reductions by hydrogen ( $\text{H}_2$ -TPR) were carried out in 5 vol. %  $\text{H}_2$  in Ar at a total flow rate of  $25\text{ ml min}^{-1}$ . Before the TPR runs, the samples (about 50 mg) were calcined in a stream of  $\text{O}_2$  at  $450\text{ }^{\circ}\text{C}$  for 2 h. The consumption of hydrogen was monitored by the thermal conductivity detector (TCD). For quantitative evaluation of the TPR profiles, the amount of the consumed reductant was calibrated with CuO. Reduction of gallium was monitored at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  in the range of  $20 - 1000\text{ }^{\circ}\text{C}$ .

## Catalytic Tests

The reactions were carried out in a plug-flow reactor in a steady state at atmospheric pressure. Typically, a total flow rate of reaction gas mixture was  $1\text{ l h}^{-1}$  and a catalyst weight of 0.5 g mixed with 1.5 ml of inert silicon carbide was used for each run. The feed composition was 20 vol. % propane, 40 vol. % oxygen and 40 vol. % ammonia. The reaction was measured in the temperature range of  $430 - 510\text{ }^{\circ}\text{C}$ . The catalysts were normally pre-treated with flowing helium at  $450\text{ }^{\circ}\text{C}$  for 2 h before each reaction run. The composition of products was determined with a gas chromatograph CHROM-5 equipped with TCD and FID

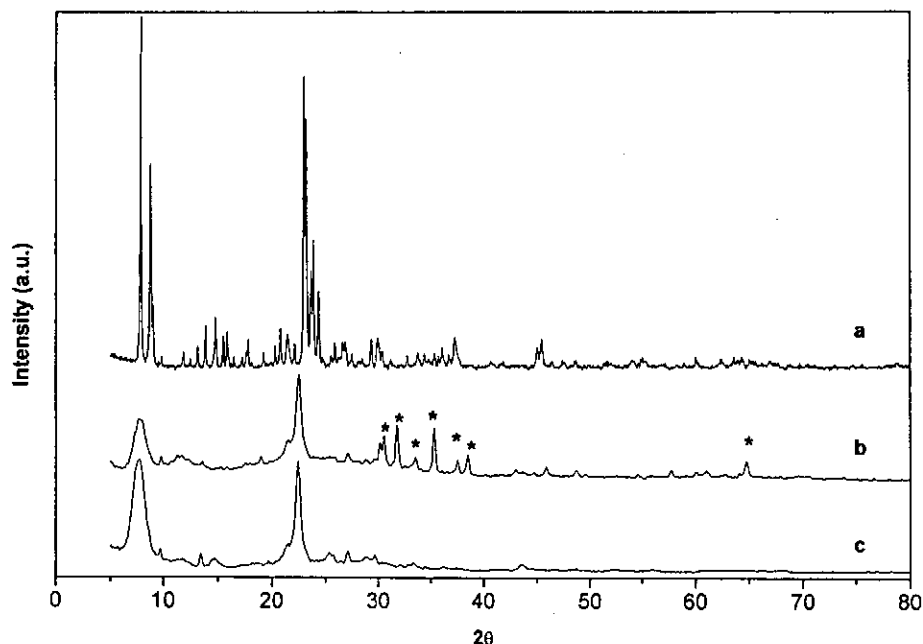


Fig. 1 The XRD patterns of Ga-zeolites: a – Ga-MFI-IE; b – Ga-BEA-SSR (\* – signals ascribed to orthorhombic  $\text{Ga}_2\text{O}_3$ ); c – Ga-BEA-CVD

detector. The hydrocarbons, nitriles, carbon dioxide and nitrogen oxides were separated by a packed column Porapak Q. Permanent gases ( $\text{N}_2$ ,  $\text{O}_2$ , CO and  $\text{CH}_4$ ) were separated by a molecular sieve 5A column. Conversion, selectivity, yield and turn-over-frequency (TOF) value were calculated on the basis of mass balance.

## Results and Discussion

The XRD pattern of all zeolite samples (see Fig. 1) show the presence of only a zeolite-type framework structure characteristic of MFI and BEA structures [33]. No evidence of damage to zeolite structure was found. Only Ga-BEA-SSR sample exhibits signals in the range of theta from 30 – 40 °, which were described on the basis of databases of XRD patterns to crystalline phase of orthorhombic  $\text{Ga}_2\text{O}_3$ . The chemical analyses performed on washed and calcined samples are reported in Table I. Ga-zeolite prepared by ion exchange from gallium nitrate solution exhibit Ga/Al ratio very close to one. XRD of Ga-MFI-IE does not exhibit presence of oxidic species in catalyst. This means that each atom of gallium is in the vicinity of one framework atom of aluminium and therefore the species of gallium must be

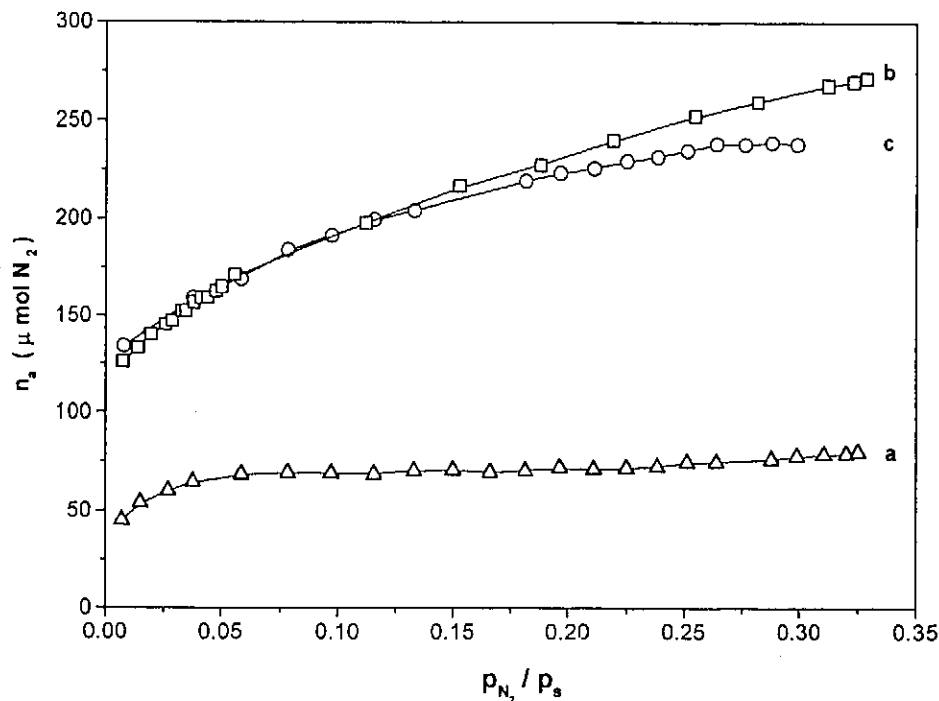


Fig. 2 The adsorption isotherms of nitrogen at 77 K: a – Ga-MFI-IE; b – Ga-BEA-SSR; c – Ga-BEA-CVD

present in zeolite in the form of gallyl ions  $(\text{GaO})^+$ .

Figure 2 shows the  $\text{N}_2$  adsorption isotherms for all the zeolite samples. It can be seen that the Ga-zeolite samples have the shape of adsorption isotherms typical of microporous materials with high specific area (for these materials see Table I). The comparison with parent materials leads to the conclusion that the adsorption capacities of zeolites after introduction of gallium decrease. As there occurred no changes in the crystallinity (see the XRD pattern), it can be concluded that the specific area decreases as the intrazeolitic space is used up to accommodate the gallium species.

The IR spectra of the Ga-zeolites in the region of OH groups are presented in Fig. 3A. The band at  $3610 \text{ cm}^{-1}$  is ascribed to vibration of hydroxyl in the Si-OH-Al groups, which correspond to Bronsted acid sites. The low intensity band at  $3660 \text{ cm}^{-1}$  reflects OH groups bound to extra-framework aluminium, a high intensity band at  $3745 \text{ cm}^{-1}$  of terminal Si-OH groups, and a low-intensity band at  $3780 \text{ cm}^{-1}$ , is tentatively ascribed to OH groups bound to “framework Al” in defects with adjacent Si-OH group. It is clearly seen that BEA zeolites exhibit much higher level of the dehydroxylation of Si-OH-Al groups than MFI zeolite.

Table I Chemical composition and properties of Ga-zeolites

Sample	Catalyst			N <sub>2</sub> adsorption		H <sub>2</sub> -TPR	Catalytic test
	Si/Al <sup>a</sup>	Ga/Al <sup>a</sup>	w <sub>Ga</sub> , wt. %	S, m <sup>2</sup> g <sup>-1</sup>	S <sub>r</sub> <sup>b</sup>	H <sub>2</sub> /Ga <sup>c</sup>	TOF, <sup>d</sup> h <sup>-1</sup>
Ga-MFI-IE	14.0	0.95	7.19	94	0.52	0.523	1.4
Ga-BEA-CVD	9.5	0.10	0.93	361	0.72	0.98	10.1
Ga-BEA-SSR	12.7	1.75	14.29	374	0.67	0.115	0.9
Ga <sub>2</sub> O <sub>3</sub>	-	-	-	61	-	-	-

a – atomic ratios

b – relative surface, surface of catalysts compared with the parent zeolite

c – molar ratio of consumed hydrogen up to 1000 °C in TPR experiment and gallium ions in the TPR reactor

d – TOF (turn over frequency), number of converted molecules of propane per one gallium ion per hour

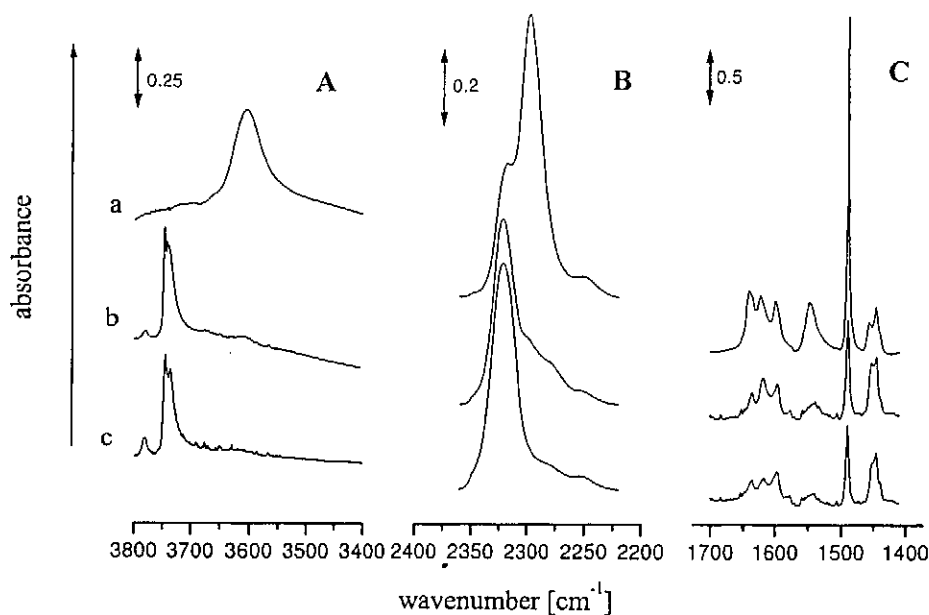


Fig. 3 The infrared spectra of Ga-zeolites: A) Region of the OH groups of dehydrated Ga-zeolites before adsorption of probe molecules; B) Ga-zeolites after adsorption of 0.5 kPa of d<sub>3</sub>-acetonitrile and desorption at RT; C) Ga-zeolites after 0.5 kPa of pyridine adsorbed and evacuated at RT; a – Ga-MFI-IE, b – Ga-BEA-SSR, c – Ga-BEA-CVD



It is induced by the instability of the BEA matrix at higher temperatures. The great intensity of the band at  $3745\text{ cm}^{-1}$  is connected with very small dimension of crystal in comparison with MFI zeolite. This is in accordance with the width of signals in XRD patterns of these materials. The studies of the acid properties of Ga-zeolite samples according to the infrared spectra of adsorbed pyridine and  $d_3$ -acetonitrile ( $CD_3CN$ ) indicate the presence of Lewis and Brønsted acid sites. The chemisorbed pyridine on Ga-BEA and Ga-MFI (Fig. 3B) is identified by the usual set of bands: two bands at  $1454$  and  $1624\text{ cm}^{-1}$  (or  $1623\text{ cm}^{-1}$  for Ga-MFI) are related to Lewis-bonded pyridine (PyL), two bands at  $1546$  and  $1635\text{ cm}^{-1}$  (or  $1547$  and  $1636\text{ cm}^{-1}$  for Ga-MFI) are assigned to pyridinium ions ( $PyH^+$ ) and the superposition of signals of both adsorbed species at  $1490\text{ cm}^{-1}$  ( $PyL + PyH^+$ ). The number of Lewis sites increases as that of the Brønsted sites decreases upon introduction of Ga ion. The IR spectra of interaction complexes of  $CD_3CN$  with Ga-containing zeolites after evacuation at RT are given in Fig. 3C. The adsorption of  $CD_3CN$  on Ga-BEA and Ga-MFI gives rise to the formation of a series of IR bands. Four bands at  $2322$ ,  $2297$ ,  $2265$  and  $2250\text{ cm}^{-1}$  can be seen. According to the literature data [27], the bands at  $2322$  and  $2297\text{ cm}^{-1}$  (CN vibration) can be correlated to the adsorption on Lewis aluminum sites (AL) and bridging OH groups (AB). The band at  $2265\text{ cm}^{-1}$  is attributed to physical adsorption of  $CD_3CN$  (physisorb). The band related to the vibration of  $CD_3$  at  $2250\text{ cm}^{-1}$  is also present. All the infrared spectra bring evidence that MFI zeolite exhibits much higher number of Brønsted acid sites than BEA zeolites.

Figure 4 shows the TPR patterns of Ga-zeolites. It is clearly seen that reduction of gallium ion runs at temperatures higher than  $400\text{ °C}$  and reduction is not complete quantitatively at  $1000\text{ °C}$ . No reduction was observed in the case of bulk  $Ga_2O_3$  up to  $1000\text{ °C}$  (see Fig. 4 d). This is in accordance to the data reported in literature [34]. The data obtained from TPR pattern of Ga-zeolites indicate that bare gallium ions or oxo-complexes of gallium coordinated to zeolite framework are more easily reducible than bulk gallium oxide. From quantitative analysis of TPR curves (see Table I) results that Ga-BEA-CVD samples contain gallium mainly in the form of gallyl ions  $(GaO)^+$  (which are reducible), whereas the Ga-MFI-IE sample exhibits only half of the gallium at the cationic sites and the rest of gallium is in the form of bulk oxide. The Ga-BEA-SSR sample exhibits only small rate of hydrogen consumption, which indicates that the major part of gallium is in the form of  $Ga_2O_3$ . This is due to the excess of oxide in the physical mixture or insufficient interaction of gallium ions with Brønsted acid sites of zeolite during reductive solid state reaction.

The ammoxidation of propane over Ga-zeolites mainly leads to formation of propene and carbon oxides. Acetonitrile, acrylonitrile and traces of acrolein were detected as minor products. A relatively great amount of propene in the products indicates that insertion of nitrogen into hydrocarbon is the rate-limiting step. Figure 5 shows the effect of temperature for the Ga-BEA-CVD catalyst. An

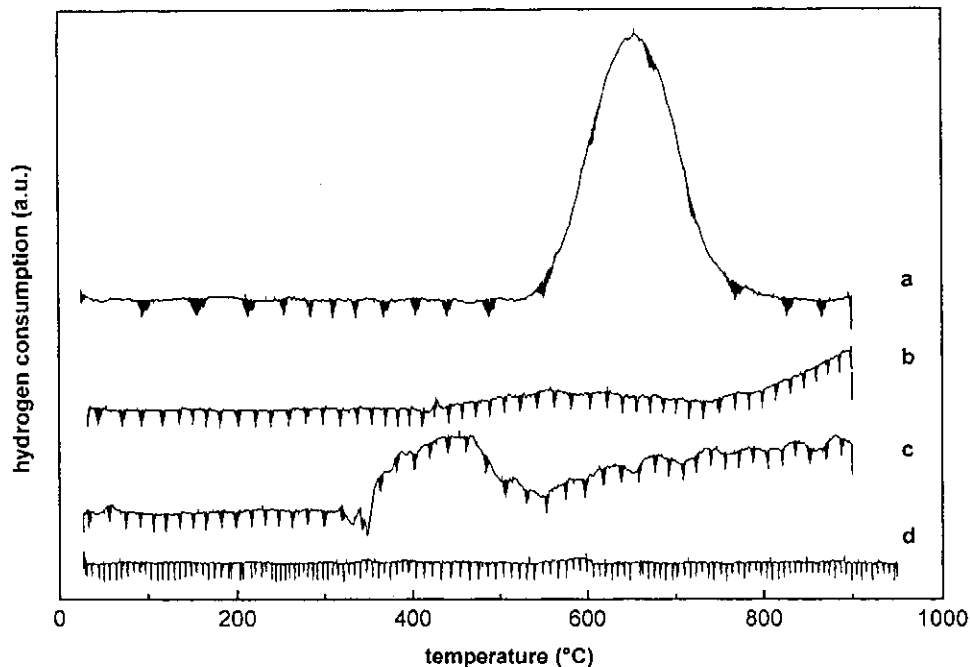


Fig. 4 The TPR pattern of Ga-zeolites: a – Ga-MFI-IE; b – Ga-BEA-SSR; c – Ga-BEA-CVD; d –  $\text{Ga}_2\text{O}_3$

increase in the temperature from 450 to 510 °C increases the conversion from 8 to 33 %. This observation is not surprising because higher temperature facilitates the activation of C-H bonds. However, the selectivity to propene and acrylonitrile decreases and the selectivity to carbon monoxides and acetonitrile increases. The increasing temperature thus promotes not only the activation and ammoxidation of propane, but also the formation of  $\text{CO}_x$ . The selectivity to acrylonitrile is lower than the selectivity to acetonitrile in all the cases. It is caused by the Markovnikov addition of ammonia to propene [35] or acrylonitrile ammonolysis [19,20]. The comparison of catalytic activity of Ga-zeolites prepared by different methods in amoxidation of propane at 450 °C is summarized in Table II. The highest catalytic activity was found with the sample prepared by chemical vapour deposition method. The zeolites prepared by ion exchange from solution and by solid state reaction exhibit lower activities. This means that gallium ions coordinating to zeolite framework are more active than oxidic gallium. The very low activity of Ga-BEA-SSR can be caused by low level of ion exchange and/or very low specific surface area of non-porous bulk gallium oxide.

All the above results prove that Brønsted acid sites play a role in synergy

with gallium species. The presence of zeolitic protons enhance reducibility of gallium ions and enhance catalytic activity of Ga ions in the transformation of propane in the presence of ammonia and oxygen.

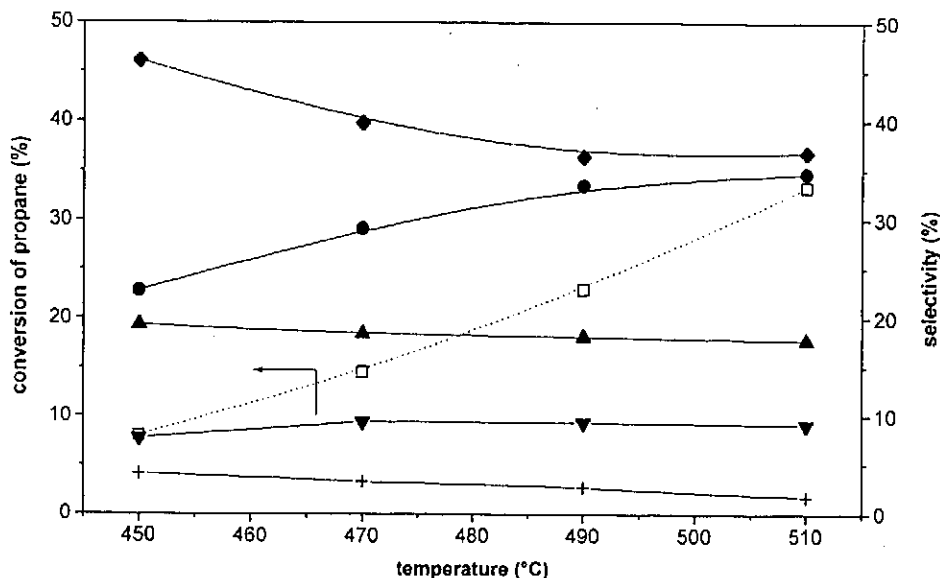


Fig. 5 The conversion of propane and selectivity to products in ammoxidation of propane over Ga-BEA-CVD sample as a function of temperature. Conditions:  $m_{cat} = 0.5$  g,  $F = 1$  l h<sup>-1</sup>,  $C_3H_8O_2/O_2/NH_3 = 20/40/40$ ,  $\square$  - the conversion of propane,  $\bullet$  - selectivity for CO,  $\blacklozenge$  - propene selectivity,  $\blacktriangle$  - CO<sub>2</sub> selectivity,  $\blacktriangledown$  - acetonitrile selectivity,  $+$  - acrylonitrile selectivity

Table II Catalytic performance of Ga-zeolites for ammoxidation of propane at 450°C

Catalyst	Conversion, %				Selectivity, %				TOF, h <sup>-1</sup>
	C <sub>3</sub> H <sub>8</sub>	O <sub>2</sub>	NH <sub>3</sub>	CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>3</sub> N	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>3</sub> N	
Ga-MFI-IE	8.7	32.8	18.5	39.5	12.9	9.4	29.2	9.0	1.4
Ga-BEA-CVD	8.0	29.7	7.8	22.8	19.3	7.7	46.1	4.1	10.1
Ga-BEA-SSR	11.1	39.7	20.4	15.5	28.5	16.3	38.1	1.6	0.9

## Conclusion

The aim of this study was to investigate redox and acid-base properties and catalytic activity in ammoxidation of propane of gallium species generated into MFI and BEA zeolite matrices by different methods. The conclusions resulting from our experiments are:

- i Incorporation of gallium leads to a decrease in specific surface of zeolite catalysts without any change in crystallinity.
- ii The interaction of gallium species depends on the preparation method. The best incorporation of gallium into cationic sites was achieved by chemical vapour deposition method. Ion exchange from gallium nitrate solution and solid state reaction H-zeolite with  $\text{Ga}_2\text{O}_3$  lead to formation of extraframework oxide clusters.
- iii Main products of ammoxidation of propane over Ga-zeolites are propene and less carbon oxides. Acetonitrile and acrylonitrile is formed too.
- iv Formation of acetonitrile proceeds most likely during the addition of ammonia to propene molecule, but if acrylonitrile were formed, it would be decomposed to acetonitrile.
- v The activity sequence of Ga-zeolites in ammoxidation of propane is: Ga-BEA-CVD  $\gg$  Ga-MFI-IE  $>$  Ga-BEA-SSR
- vi Bulk gallium oxide is inactive in the ammoxidation of propane. Most likely the active sites are species which are able to reduce by hydrogen up to 1000 °C. These species are coordinated to negative charge of zeolite matrix probably as a gallyl ions  $(\text{GaO})^+$ .

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