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Preparation of In,H-ZSM-5 for DeNOx reactions by solid-state ion exchange

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ABSTRACT

A simple method is proposed to prepare In,H-ZSM-5 catalyst for DeNOx reactions. This consists of mechanically mixing the fine powders of In_2O_3 and H-ZSM-5 followed by heating in oxygen free inert gas flow to 580 °C where indium undergoes thermal auto-reduction and moves into exchange positions as In^+ without destroying the crystalline structure of the zeolite.

It was evidenced by IR, temperature-programmed reduction (TPR) and reoxidation that, once In^+ was introduced into the lattice either by reductive solid-state ion exchange (RSSIE) or by thermal auto-reductive SSIE, it can be oxidized by O_2 or in the DeNOx reaction to $(InO)^+$. The formed $(InO)^+$ can easily be reduced to In^+ suggesting that In,H-ZSM-5 might be a good catalyst for reactions where a redox cycle in the catalyst is involved in the reaction mechanism.

Selective catalytic reduction (SCR) by methane proved that only a small fraction of In exchanged, together with some acid sites of the zeolite formed the active center for the catalytic reaction. XRD, XPS and FT-IR using pyridine proved that the structure of the zeolite and these centers are stable under reaction conditions and In is mainly in the form of $(InO)^+$ in the used catalyst.

1. Introduction

Cation exchange between zeolites and aqueous salt solutions, the so-called “conventional” ion exchange has several disadvantages. The equilibrium constants and, hence, the ion-exchange degrees depend on: (i) the size and valence of both the in-going and out-going cations, (ii) the structure of the zeolite, and (iii) the presence or absence of ligand molecules (i.e. bulky solvated cations are not able to penetrate into small-pore zeolites because of geometric restraints). Thus, in most cases only more or less partial ion exchange is achieved after establishment of the equilibrium. The ion-exchange procedure has to be repeated several times in order to obtain high exchange degree. Hence, conventional ion exchange of zeolites is a time-consuming procedure and produces relatively large amounts of waste solutions.

From the mid-eighties solid-state techniques for ion exchange (SSIE) in zeolites were applied for the exchange of cations between the ground mixtures of zeolite crystallites and crystalline metal salts or metal oxides at higher temperatures in the absence of liquid water. The method proved to be free of the restrictions of the conventional ion-exchange process. If the reaction product is volatile SSIE equilibrium shifted to the formation of metal cation-form of the zeolite. Any ion-exchange degree can be achieved simply by mixing an adequate amount of the compound of the in-going cation with the starting zeolite. Recently, an excellent review was published by Karge and Beyer [1] on the modifications of cation populations in zeolite by SSIE.

For ground mixture of Ga_2O_3 and In_2O_3 with H-zeolites, Kanazirev et al. [2–4] reported a special variety of this method named “reductive solid-state ion exchange” (RSSIE) wherein the thermal treatment is performed in hydrogen atmosphere and the in-going cation is reduced and incorporated in the lower oxidation state. The exchange processes were assumed to occur in two steps according to:

$$M_2O_3 + 2H_2 \rightarrow M_2O + 2H_2O \quad (1)$$

$$M_2O + 2H^+Z^- \rightarrow 2M^+Z^- + H_2O \quad (2)$$

wherein Z^- represents the fraction of the zeolite possessing one negative charge. They also stated that at the same temperature, no exchange reaction involving trivalent gallium or indium species proceeds in inert atmosphere. Our results of the detailed studies on RSSIE of indium into the NH_4-Y,FAU, NH_4-Beta and H-mordenite supported these conclusions [5–7]. We also proved that not only H_2, but CO and NH_3 released from the mixture of In_2O_3 and NH_4-zeolites, also induced RSSIE [8]. In addition, in case of as-synthesized zeolite Beta the thermal decomposition products of

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the template resulted in the incorporation of univalent indium into the lattice [9].

In contrast, Ogura et al. [10] and Zhou et al. [11] supposed, that cationic trivalent indium species $(InO)^+$ were introduced into the zeolite directly by conventional solid-state ion exchange from the ground mixture of In_2O_3 and H-ZSM-5 (Eq. (3)) upon thermal treatment in inert atmosphere.

$$In_2O_3 + 2H^+Z^- \rightarrow 2(InO)^+Z^- + H_2O \qquad (3)$$

These species were regarded as catalytically active sites in the reduction of NO_2 and NO with methane in the presence of oxygen. Reduction of the In^{3+} ions of the bulk In_2O_3 was not supposed during the solid-state process. It was proved that monovalent indium cation can be obtained in a second step, when the introduced $(InO)^+$ cation is reduced according to:

$$(InO)^+Z^- + H_2 \rightarrow In^+Z^- + H_2O \qquad (4)$$

More recently, we found that monovalent indium is incorporated into the cationic positions of high-silica zeolite, i.e. H-ZSM-5 upon treatment in high vacuum (HV) at 570 °C [12]. The process is named as auto-reductive solid-state ion exchange (AR-SSIE). It was evidenced that the initial step is the auto-reduction of In_2O_3 to In_2O under release of oxygen then the subsequent reaction is solid-state ion exchange between the In^+ ions and the zeolitic protons according to:

$$In_2O_3 + 2H^+Z^- \rightarrow 2In^+Z^- + H_2O + O_2 \qquad (5)$$

In the present work further evidence was provided for the process of AR-SSIE in the mechanical In_2O_3/H-ZSM-5 mixtures treated in HV or inert atmosphere. Redox behavior of the cationic indium species introduced by RSSIE or AR-SSIE was also investigated by temperature-programmed reduction (TPR) and Fourier-transform infrared (FT-IR) spectroscopy using pyridine. The mixtures with different indium contents, pretreated in inert atmosphere, were found to be active in the reduction of NO with methane in the presence of oxygen. The effect of indium content on the activity of the catalysts was also studied. Before and after catalytic run samples were characterized by X-ray diffractometry, X-ray photoelectron spectra (XPS) and FT-IR spectroscopy using pyridine.

2. Experimental

2.1. Materials

The parent H-ZSM-5 zeolite was prepared according to procedure B in Ref. [13] using alkyl ammonium compounds as structure directing component. Aluminum and sodium content of the calcined material were determined by atomic absorption spectroscopy (AAS) after dissolving the solid in hydrofluoric acid. The aluminum and sodium content of the zeolite were 0.52 and 0.02 mmol/g, respectively. The Si/Al ratio of the sample was 31. Concentration data are related to material calcined at 1000 °C.

In order to determine the amount of protons which can be exchanged in the zeolite sample the ammonium-form of the calcined material was prepared. Conventional ion-exchange process was applied using 1 M NH_4Cl solution at room temperature.

For the preparation of the In,H-ZSM-5 catalysts the H-form of the ZSM-5 zeolite was mixed in an agate mortar with a high purity In_2O_3 (99.99%, Aldrich) in amounts corresponding to molar In/H^+ ratios of 1, 1/3, 1/5, 1/10, 1/20 and 1/40. The powder mixtures were pressed into pellets with a pressure of 130 MPa then crushed and sieved. The 0.25–0.5-mm particles were used for the TPR and the catalytic experiments. For some experiments Na-ZSM-5 and In_2O_3/Na-ZSM-5 samples were prepared in the same way.

2.2. Methods

The NH_4^+-exchanged sample was characterized by temperature-programmed ammonia evolution (TPAE) measurements. About 300 mg of sample were heated from 150 to 650 °C at a rate of 10 °C/min in a 20-ml/min flow of dry nitrogen. From the effluent NH_3 was absorbed in distilled water. The pH of the absorbing solution was kept between pH 5.5 and 6.0 by automatically titrating the absorbed NH_3 with 0.1 M HCl solution. The ammonia, evolved from the sample between 180 and 650 °C during TPAE run, was taken as equivalent with the ion-exchange capacity (IEC) of the sample, i.e. with the proton (H^+) concentration.

Temperature-programmed reduction (H_2-TPR) was carried out exposing the sample placed in a reactor tube (6 mm I.D.) to a 20-ml/min flow of 9.7 vol.% H_2/Ar mixture. 140 mg of samples were used for the experiment. The water was removed from the reactor effluent by passing it through a dry ice trap (−68 °C). The rate of hydrogen uptake was recorded using a thermal conductivity detector (TCD). Measured amount of Cu(II)O (Merck) was reduced under the same conditions as the sample to calibrate the system for H_2 consumption.

Transmission FT-IR spectra were recorded by a Nicolet Impact Type 400 spectrometer. All spectra were collected at room temperature by 32 scans at a resolution of $2\ cm^{-1}$. Spectra were normalized to wafer thickness of $5\ mg/cm^2$. Pyridine (Py) was used for the identification of the Lewis-acid indium cations. After the respective treatment the wafer was contacted with pyridine (Py) at a Py pressure of 5.7 mbar at 200 °C and degassed at 100 °C by 30-min evacuation then a spectrum was recorded at room temperature.

X-ray diffraction (XRD) patterns of the fresh In_2O_3/H-ZSM-5 mixtures and the used catalysts were recorded using a powder diffractometer (Phillips PW 1870) applying monochromatized Cu $K\alpha$ radiation.

XPS of the fresh and used catalysts were recorded using KRATOS XSAM-800 machine with Al anode and 40 eV Pass Energy. The Si 2p peak at 103.3 eV was used for charge compensation. Sensitivity factors given by the manufacturer were used for quantification.

2.3. Catalytic reaction

160 mg sample of 0.25–0.5-mm sieve fraction was placed into a quartz plug flow reactor of 6 mm I.D. and heated in 40 ml/min Ar flow up to 580 °C using 10 °C/min rate and kept at this temperature for 2 h. The temperature was decreased to 500 °C and the flow was switched for 2% NO/Ar. The effluent was analyzed by a BALZERS PRISMA QMS connected via a differentially pumped capillary inlet system and m/e at 12, 14, 15, 18, 28, 30, 32 36, 44 and 46 were recorded. The fragmentation patterns of the pure components were used in the quantification of the overlapping m/e values of N_2 N_2O and CO at m/e = 28, NO and N_2O at m/e = 30, CO_2 and N_2O at m/e = 44. As NO_2 at m/e = 46 was never observed, its fragmentation was not considered. The conversions of NO and CH_4 were calculated as usual by subtracting their outlet concentration from the inlet one and divided by the latter. On reaching steady-state signals the temperature was decreased to 200 °C, the flow was switched for Ar and TPD up to 580 °C was started using 10 °C/min rate. The flow was switched to the reaction mixture of 1% NO + 1% CH_4 + 2.5% O_2 with flow rate of 40 ml/min. This concentration is about an order of magnitude higher than the ones used typically for practical conditions but using 1% of NO and 1% of CH_4 the steady-state conditions could be reached in reasonable time in the

transient studies, not reported in the present work. After stabilization of the QMS signals the temperature was decreased by 5 °C/min rate to 200 °C followed by heating to 580 °C. This cycle was repeated several times. Before and after each run the QMS was calibrated by sampling the reactants from the by-pass line.

After the catalytic run samples were taken from the reactor and kept in air at room temperature then characterized by XRD, XPS and FT-IR spectroscopy using Py.

3. Results and discussion

H-zeolites or cationic precursor forms of H-zeolites are preferred for SSIE. Therefore zeolites synthesized mostly in the sodium form (e.g., Y,FAU and mordenite) have to be transformed, prior to SSIE, into the hydrogen or, e.g., ammonium-form by conventional ion exchange with acids or ammonium salts. In case of ZSM-5 there is no need for this additional step. Since the zeolite was prepared in the presence of alkyl ammonium template cations which compensate the negative framework charge in the as-synthesized form. Thus, the oxidative template decomposition results in directly the H-form of the ZSM-5 zeolite. It was revealed also by chemical analysis which showed that the sodium content of the calcined material is negligible. Without any modification this calcined form can be used for the preparation of the In_2O_3/H-ZSM-5 mixtures.

The IEC of the zeolite sample is slightly lower (0.52 mmol/g) than the bulk aluminum content (0.61 mmol/g) pointing out that part of the aluminum is in extra-framework position (EFAl).

3.1. Temperature-programmed reduction of In_2O_3/H-ZSM-5 and the oxidized In-ZSM-5

The TPR curve of the In_2O_3/H-ZSM-5 ($In/H^+ = 1$) (Fig. 1a) mixture shows that the hydrogen consumption starts at about 350 °C and proceeds with a maximum rate at about 450 °C. After reoxidation at 500 °C with O_2/He mixture a second TPR run was carried out with the same sample. The reduction starts at lower temperature, i.e. at 200 °C, in addition, the temperature maximum was also found to shift by more than 100 °C to lower temperature (Fig. 1b). The amount of H_2 consumed during the first and second reduction steps were 0.96 and 0.97 H_2/In, respectively. In order to prevent thermal dehydroxylation of the zeolite sample the reduction temperature was not increased over 550 °C.

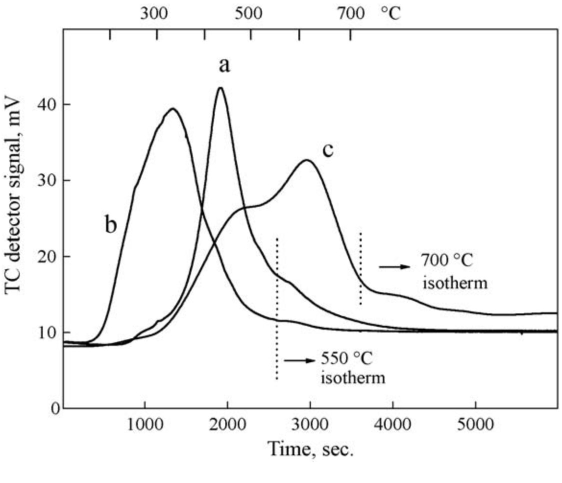

Fig. 1. TPR profile of In_2O_3/H-ZSM-5 ($In/H^+ = 1$) mixture (a), the second TPR run of the *in situ* formed and reoxidized In-ZSM-5 sample (b), and In_2O_3/Na-ZSM-5 (In/Na = 1) mixture (c). The In_2O_3/H-ZSM-5 ($In/H^+ = 1$) mixture was pretreated in a 19.2 vol.% O_2/He flow at 500 °C for 1 h and cooled down in N_2, then heated in a 9.7 vol.% H_2/Ar flow of 20 cm^3 (STP)/min with a heating rate of 10 °C/min from 50 to 550 °C and kept at the final temperature for 1 h (curve a). Then the obtained In-ZSM-5 sample was oxidized at 500 °C and reduced again (curve b). The same pretreatment and reduction conditions were applied for In_2O_3/Na-ZSM-5 (In/Na = 1) mixture (curve c) like in curve a, except the final temperature (700 °C).

The hydrogen consumption in the first TPR run is in line with the stoichiometry of Eq. (1), i.e. it corresponds to the reduction of trivalent indium to monovalent indium. The result supports that in the presence of zeolites containing Brønsted-acid sites In_2O_3 was supposed to be reduced to univalent indium which replace the zeolitic protons and In^+Z^- were formed according to:

$$In_2O_3 + 2H_2 + 2H^+Z^- = 2In^+Z^- + 3H_2O \quad (1 + 2)$$

It should be mentioned that TPR results provide evidence only for the reduction step (Eq. (1)), evidence for the subsequent ion-exchange step (Eq. (2)) will be provided by FT-IR studies of the formed cationic indium species.

Cationic In^+ can be oxidized to $(InO)^+$ cation at 500 °C by O_2 according to:

$$In^+Z^- + 0.5O_2 \rightarrow (InO)^+Z^- \quad (6)$$

This was substantiated by the amount of H_2 consumed in the second TPR run when the $(InO)^+$ cations were reduced to monovalent indium cation (Eq. (4)).

It can be seen that the reduction in the second TPR run (Fig. 1b) has been proved to proceed at temperatures at about 100 °C lower than in case of the first TPR run (Fig. 1a). This means that trivalent indium is much easier reduced in the form of $(InO)^+$ lattice cations formed in ZSM-5 zeolite upon oxidation of In^+ cations than in the form of In_2O_3. The amount of hydrogen consumed during RSSIE (Eq. (1)) and during the reduction of In-ZSM-5 (Eq. (4)) after intermediate reoxidation is, within the limits of experimental error, in full agreement with the stoichiometry of the respective equation. We came to the same conclusions for In_2O_3/NH_4-Beta ($In/NH_4^+ = 1$) mixture [6]. These results are in agreement with the findings of Zhou et al. [11] and Sowade et al. [20].

After the above treatments the sample was reoxidized again at 500 °C with O_2 and a third TPR run was performed. During this step about one hydrogen molecule per indium atom consumed substantiating that reactions (4) and (6) describe a fully reversible cycle.

The reversible changes of the oxidation state of indium lattice cations ($In^+ \leftrightarrow (InO)^+$) makes the In,H-ZSM-5 a good candidate for catalyst in DeNOx reactions as there is a general agreement that a good catalyst has to undergo redox cycles.

TPR curve of In_2O_3/Na-ZSM-5 (In/Na = 1) (Fig. 1c) shows that hydrogen consumption started at the same temperature (about 350 °C) like in presence of the H-form (Fig. 1a) and finished up to 700 °C. The hydrogen consumption was found to be 1.45 H_2/In, which correspond to the reduction of indium(III)-oxide to metallic indium according to:

$$In_2O_3 + 3H_2 \rightarrow 2In^0 + 3H_2O \quad (7)$$

This result proved that upon thermal treatment in H_2 ion exchange between indium and sodium cations does not take place in the physical mixture of crystalline In_2O_3 and Na-ZSM-5 in accordance with the results of Kanazirev and Price [3]. When the mixture was heat-treated in inert atmosphere (in Ar) up to 580 °C, then reduced in a subsequent TPR run (not shown) the hydrogen consumption was about 1.47 H_2/In indicating that the replacement of sodium cation for indium does not occur upon thermal treatment in inert atmosphere. In the absence of zeolitic protons indium(III)-oxide was reduced to metallic indium (In^0).

Table 1
Hydrogen consumption during the reduction of In-ZSM-5 oxidized at increasing temperatures. In-ZSM-5 were prepared *in situ* by RSSIE from In_2O_3/H-ZSM-5 (In/H^+ = 1) mixture. Sample pretreatment and the TPR run was detailed in the legend of Fig. 1. Fresh mixtures were used in each redox cycle. H_2/In = 1 corresponds to the stoichiometry of the reduction ($InO^+Z^- + H_2 \rightarrow In^+Z^- + H_2O$).

Oxidation temperature (°C)	Hydrogen consumption during TPR run (H_2/In)
150	0.22
300	0.44
450	0.93
500	0.97

3.2. Oxidation of In^+ to $(InO)^+$ by O_2

In order to determine the temperature needed for complete oxidation of In^+ cation introduced by reductive solid-state ion exchange, the In-ZSM-5 (In/H^+ = 1) samples were oxidized with a O_2/He flow at increasing temperatures and then in a subsequent reduction step the hydrogen consumption was measured (Table 1). It is evident if all In^+ cation is oxidized to $(InO)^+$ the hydrogen consumption is one molecule hydrogen per indium atom. H_2/In values of lower than one indicates that partial oxidation proceeds in O_2/He mixture at lower temperatures than 500 °C. The higher the temperature the higher the fraction of In^+ which was converted to $(InO)^+$ cations (Table 1).

It should be mentioned that comparing to the other zeolites (such as, zeolite-Y, Beta, mordenite) in the MFI structure relatively high temperature needed for the complete oxidation of monovalent indium cation in O_2/He stream. In^+ cation occupying lattice cationic positions in Y,FAU(Si/Al = 2.5) type zeolite can be oxidized with O_2 very easily. The oxidation starts at about 50 °C and finishes up to 150 °C. The reaction was found to be strongly exothermic [14]. Results suggest that the mechanism of the oxidation of In^+ to $(InO)^+$ proceeding with molecular oxygen are different on the two zeolites. The concentration of the framework aluminum, i.e. the distance of the cationic positions actually occupied by In^+ ions may play a decisive role in the oxidation mechanism. Naturally, the rate determining step of the oxidation reaction is the dissociation of the oxygen molecules involving four electrons.

It seems that in presence of high concentration of In^+ ions (Y,FAU(Si/Al = 2.5) zeolite) In^+ ions interact with oxygen molecules in pairs. Two In^+ ions activate one O_2 molecule, probably, via peroxide mechanism according to:

$$2In^+ + O_2 \rightarrow \{In_2{}^{(1+\delta)+}O_2{}^{(2+2\delta)-}\} \quad (8)$$

In contrast, in a high-silica zeolite (such as ZSM-5 (Si/Al = 31)) with the low concentration of In^+, isolated In^+ ions interact with the oxygen molecules, i.e. one In^+ ion with one oxygen molecule and the following intermediate can be formed:

$$In^+ + O_2 \rightarrow \{In^{(1+\delta)+}O_2{}^{(2+\delta)-}\} \quad (9)$$

Thus, the low-temperature oxidation of In^+ to $(InO)^+$ with O_2 was supposed to proceed via peroxide intermediate represented by Eq. (8). The initial step of the high-temperature oxidation, however, can be described by Eq. (9).

In case of zeolites, such as mordenite (Si/Al = 6.5) and zeolite Beta (Si/Al = 12.8) possessing higher Si/Al ratio than Y,FAU(Si/Al = 2.5) but lower than ZSM-5 zeolite, we found that the oxidation of In^+ cations proceeded at about 400 °C [7].

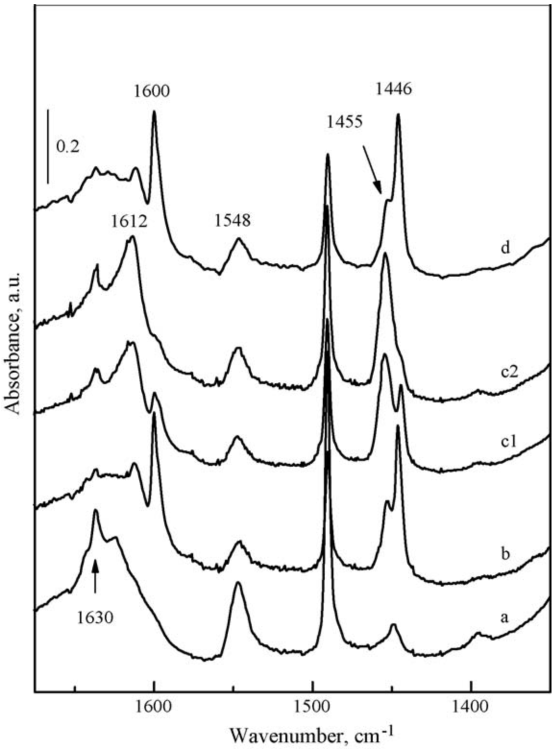

Fig. 2. FT-IR spectra of pyridine adsorbed on H-ZSM-5 (a) and In_2O_3/H-ZSM-5 (In/H^+ = 1) mixture (b–d) subjected to the following subsequent treatments: (a) evacuation in HV at 450 °C for 0.5 h; (b) reduction in 200 mbar H_2 at 450 °C for 0.5 h then evacuation at 300 °C in HV for 15 min; (c) oxidation in 200 mbar O_2 at 400 °C (c1) or 450 °C (c2) for 0.5 h then evacuation at 200 °C in HV for 15 min; (d) reduction in 200 mbar H_2 at 450 °C for 0.5 h then evacuation at 300 °C in HV for 15 min. After each treatment sample was contacted with pyridine. In each run fresh wafer was used.

3.3. Fourier-transform infrared studies of reductive SSIE, In^+ oxidation and $(InO)^+$ reduction

Fig. 2 shows the spectra of pyridine adsorbed on the parent H-ZSM-5 zeolite after thermal activation at 450 °C in HV and the In_2O_3/H-ZSM-5 (In/H^+ = 1) subjected to the following subsequent treatments: (i) reduction by H_2 at 450 °C, (ii) oxidation by O_2 at 400 or 450 °C and (iii) reduction by H_2 at 450 °C.

Earlier we proved that In^+ and $(InO)^+$ cations located at cationic lattice sites of zeolites could be detectable and distinguishable by typical bands at 1446(1600) and 1455(1612) cm^{-1} which were attributed to the 19b(8a) ring vibrations of adsorbed pyridine interacting with the respective cation [7]. Thus, Eqs. (1 + 2), (4) and (6) could be substantiated by the following IR results: bands typical of Py → In^+ interaction appeared at 1446(1600) cm^{-1} after reductive SSIE in stoichiometric In_2O_3/H-ZSM-5 mixture and the intensity of the bands at 1548(1630) cm^{-1} attributed to 19b(8a) ring vibrations of pyridinium ions and, hence, associated with acid sites decreased (cf. a and b in Fig. 2). After subsequent oxidation with O_2 at 400 °C the intensity of the band at 1446(1600) cm^{-1} significantly decreased and new bands attributed to Py → $(InO)^+$ developed at 1455(1612) cm^{-1} (Fig. 2c1) proving that the oxidation of In^+ to $(InO)^+$ was not complete at this temperature. At 450 °C this oxidation step proceeds further because no bands can be seen at 1446(1600) cm^{-1} attributed to Py interacting with monovalent indium cation (Fig. 2c2). When the sample was treated again in hydrogen, the bands at 1446(1600) cm^{-1} were restored at the expense of the 1454(1615) cm^{-1} bands (Fig. 2d) representing that $(InO)^+$ was reduced to In^+ (Eq. (4)). The 1455-cm^{-1} band in

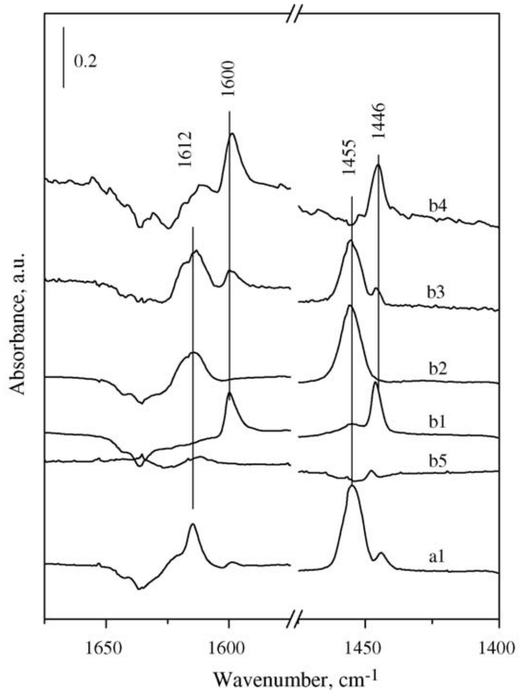

Fig. 3. Difference spectra for the parent H-ZSM-5 (a1) or In_2O_3/H-ZSM-5 ($In/H^+ = 1$) (b1–b5) mixture. The spectrum of pyridine adsorbed on the respective sample was subtracted from that adsorbed on the 400 °C-activated (in HV for 0.5 h) parent zeolite. The following subsequent treatments were applied: (a1 and b1) evacuation in HV at 500, 540 and 570 °C for 0.5 h; (b2) oxidation in 200 mbar O_2 at 450 °C for 0.5 h then evacuation at 200 °C in HV for 15 min (b3) evacuation in HV at 500 °C for 0.5 h; (b4) evacuation in HV at 570 °C for 0.5 h. (b5) The mixture was activated at 350 °C in HV for 0.5 h and 5 mbar O_2 was introduced into the cell and the temperature was maintained at 500, 540 and 570 °C for 0.5 h then evacuated at 200 °C in HV for 15 min. In each run fresh wafer was used.

spectra b and d may be attributed to extra-framework aluminum species (*vide infra*) found to be present in the parent ZSM-5 zeolite.

We also proved from the release of pyridine with increasing temperatures, that $(InO)^+$ cation represent substantially stronger Lewis-acid sites than In^+ cation [5–7,12].

3.4. Fourier-transform infrared studies of auto-reductive SSIE and auto-reduction of $(InO)^+$

Fig. 3 shows difference spectra for the parent H-ZSM-5 (a1) and In_2O_3/H-ZSM-5 ($In/H^+ = 1$) (b1–b5). From the spectrum of pyridine adsorbed on the respective sample the spectrum of pyridine adsorbed on the parent zeolite activated at 400 °C in HV for 0.5 h was subtracted. Thus, any changes in the spectra of the sample are due to the effect of the respective treatment. In this case, if the zeolite OH concentration decreases the pyridinium bands at 1548(1635) cm^{-1} appears as negative bands in the spectrum. In the spectrum of the H-ZSM-5 sample upon evacuation in HV at 570 °C new bands appear at 1455 and 1612 cm^{-1} which are attributed to the 19b(8a) vibrations of Py adsorbed on extra-framework aluminum (EFAl) species (Fig. 3a1). It evidences that considerable lattice degradation proceeds upon evacuation in HV. When the In_2O_3/H-ZSM-5 ($In/H^+ = 1$) mixture were treated the same way, bands at 1446(1600) cm^{-1} typical of Py interacting with In^+ appear in the spectrum (Fig. 3b1). The process can be described by Eq. (5) [12]. Auto-reduction of In_2O_3 to In_2O should proceed under release of stoichiometric amount of O_2 then the formed In^+ ions exchange the protons. From the decrease of the OH concentration (not shown) about 60% of exchange degree was calculated. Although the ion exchange was not complete no bands typical of Py on EFAl appear in the spectrum indicating that this In,H-ZSM-5 sample was stable towards high vacuum at 570 °C. On the one hand, In^+ cations prevent thermal dehydroxylation of the zeolite. On the other hand, zeolite stabilizes indium as lattice cation because the reduction of indium stops at monovalent oxidation state. After such treatments metallic indium was not detected by XRD in the sample.

When the thermal treatment was carried out in the presence of O_2 there was no change in the spectrum of the In_2O_3/H-ZSM-5 mixture (Fig. 3b5). AR-SSIE was completely suppressed by O_2 which evidences that the reaction should proceed according to Eq. (5).

If indium should incorporate into the zeolite as trivalent indium, i.e. $(InO)^+$ ions, O_2 should not affect the process. Thus, the mechanism described by Eq. (3) can be excluded at this temperature. It should be mentioned that in the presence of O_2 the thermal dealumination of the zeolite structure was also suppressed. The experiments for the explanation of this phenomenon are in progress.

Although the bands of Py interacting with $(InO)^+$ and the bands due to the EFAl appeared at the same wavenumbers (cf. in Fig. 3a1 and b2), they can be easily distinguished from each other by reduction with H_2 at high temperature. Upon reduction the spectrum of the H-ZSM-5 sample (Fig. 3a1) does not change (not shown). However, $(InO)^+$ can be reduced to In^+ evidenced by the disappearance of bands at 1455(1612) cm^{-1} and the reappearance of the bands at 1466(1600) cm^{-1} (cf. in Fig. 2c2 and d, *vide supra*).

When the oxidized In,H-ZSM-5 sample was evacuated in HV at 500 °C the intensity of the bands at 1455(1612) cm^{-1} typical of $Py \rightarrow (InO)^+$ decreased and concomitantly bands at 1466(1600) cm^{-1} due to $Py \rightarrow In^+$ appeared in the spectrum (Fig. 3b3). Upon evacuation at higher temperature (at 570 °C), however, the bands at 1455(1612) cm^{-1} completely disappeared and the intensity of the bands at 1466(1600) cm^{-1} increased (Fig. 3b4). Results proved that at 500 °C partial auto-reduction of $(InO)^+$ cation was found to occur according to Eq. (10), meanwhile, at 570 °C the process was complete.

$$(InO)^+Z^- \rightarrow In^+Z^- + 0.5O_2 \qquad (10)$$

3.5. Decomposition and SCR of NO

As explained in Section 2 first the mechanical mixture was heated in Ar to facilitate the ion-exchange via auto-reduction. This was followed by measuring the NO decomposition reaction using 2% NO/Ar. The QMS signals during first contact to NO are given in Fig. 4. The delay in the O_2 signal proved that In was in the form of In^+ as O_2 formed in the NO decomposition was consumed to oxidize In^+ during the first 700 s. In steady-state conditions at 500 °C the NO conversion was only 4% showing that In,H-ZSM-5 is not a good catalyst for the decomposition of NO.

TPD of NO after NO decomposition given in Fig. 5 shows that in contrast to Cu-ZSM-5 only NO and practically no O_2 was desorbing. This indicates that in the case of In,H-ZSM-5 the nitrate like intermediates were not present.

SCR using CH_4 as reductant is given in Fig. 6. In this reaction only CO_2 and N_2 were formed. Without NO, H-ZSM-5 practically does not burn methane below 500 °C, whereas NO conversion in SCR passes through a maximum at about 450 °C. This suggests that methane is attacked by intermediates formed from NO and not the reverse process is effective. The role of the intermediates is evidenced by the fact that NO alone practically does not

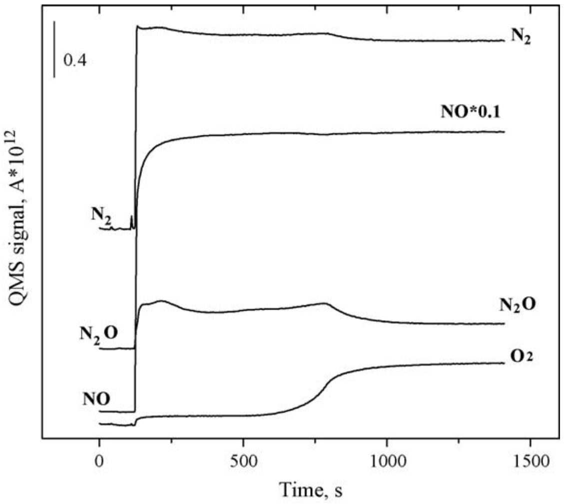

Fig. 4. First contact to 2% NO/Ar at 500 °C after SSIE. In_2O_3/H-ZSM-5 (In/H$^+$ = 1) sample. 4% NO conversion at steady state.

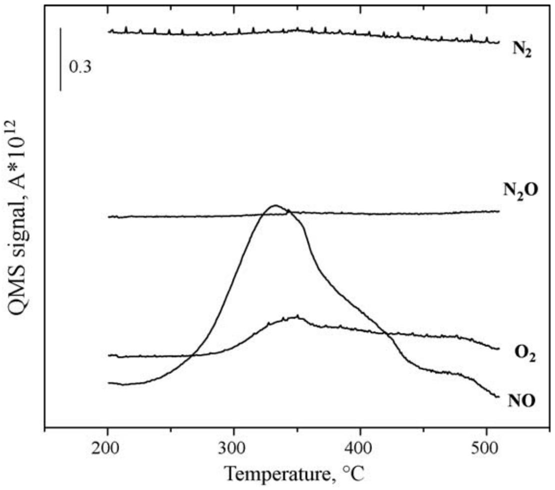

Fig. 5. TPD after NO decomposition, In_2O_3/H-ZSM-5 (In/H$^+$ = 1) sample.

decompose at 450 °C. Once the intermediates form from NO they initiate the oxidation of methane and the concentration of indium has only a marginal effect on the methane conversion. If SSIE is not possible as it happens in the case of In_2O_3 + Na-ZSM-5, there is only a negligible NO conversion proving that In_2O_3 alone is inactive. Also acidic sites alone are of low activity. Indium increases the conversion of NO above 400 °C even in low concentration but above In:H$^+$ = 1:5 there is hardly any improvement. This proves that a co-operation between In exchanged and the acidic sites is essential.

3.6. FT-IR, XRD and XPS characterization of the used NO catalysts

The In,H-form of the ZSM-5 zeolite was prepared *in situ* in the catalytic reactor by heating the In_2O_3/H-ZSM-5 mixtures (In/H$^+$ ratios of 1, 1/3, 1/5, 1/10, 1/20 and 1/40) in a flow of Ar up to 580 °C. After catalytic runs the catalysts were cooled down in the reactants and were taken from the reactor and kept in air then the FT-IR experiments were performed. Fig. 7 shows that in most cases after thermal activation of these samples in HV at 300 °C bands at 1455(1612) cm^{-1} appeared in the spectra. Knowing that these bands can be attributed to (InO)$^+$ or/and EFAl (e.g., (AlO)$^+$) species, *vide supra*, the samples were reduced with H_2 at 400 °C and these bands were found to disappear and bands typical of Py → In$^+$ interaction appeared at 1446(1600) cm^{-1} (not shown). Thus, the used In,H-ZSM-5 catalysts contains (InO)$^+$ cations but they do not contain EFAl, suggesting that indium was incorporated into as lattice cations and the release of framework aluminum is negligible.

Indium was identified as (InO)$^+$ cations which do not mean that non-reductive solid-state ion exchange proceeded according to Eq. (3). Upon heat treatment in Ar at 580 °C indium incorporated into the cationic positions as In$^+$ by auto-reductive SSIE (Eq. (5)) and it was oxidized to (InO)$^+$ by the reactants.

In$^+$ cation is not stable in air. It could be detectable only in HV in the absence of oxygen (Section 3.3). Attempts were made to distinguish the two cationic forms (i.e. In$^+$ and (InO)$^+$) by means of perturbed angular correlation (PAC) technique in the In,H-ZSM-5, In-FER [15] and In-Beta [16] prepared from In_2O_3/H-zeolite mixture by RSSIE. The PAC spectrum of the reduced sample was found to differ considerably from that of the oxidized one, the effect was explained by the formation of liquid metallic indium or nanosized In_2O_3 crystallites or by the interaction between the reductant (H_2) and the formed cation.

In Fig. 8 XRD results are presented for the untreated mixture and the used catalyst for 1:5 and 1:10 In/H$^+$ ratios. It is quite clear that in the used catalyst there is no In_2O_3 present and the crystallinity of the zeolite has not changed either. This means that In moved into exchange positions and the structure of the zeolite was kept intact.

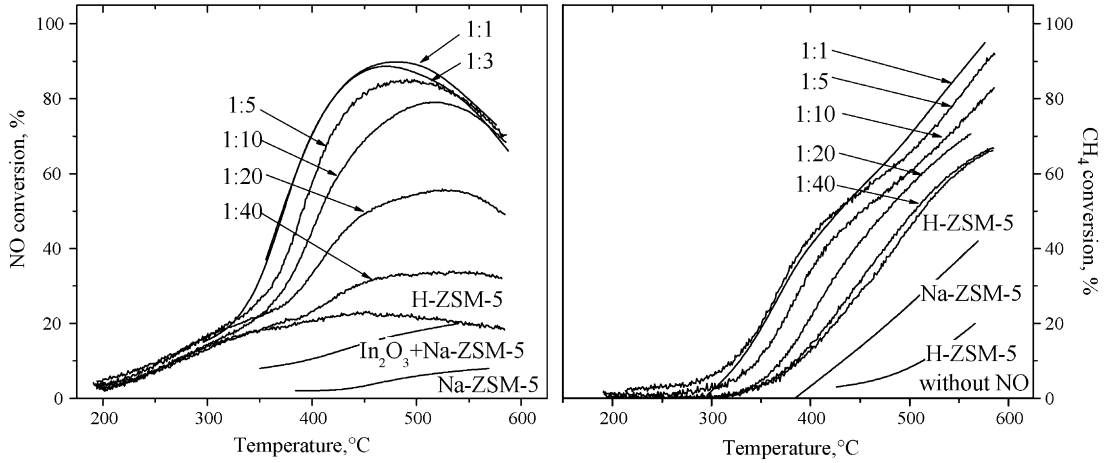

Fig. 6. NO and CH_4 conversion on different catalysts, In/H$^+$ is marked as 1:*X*.

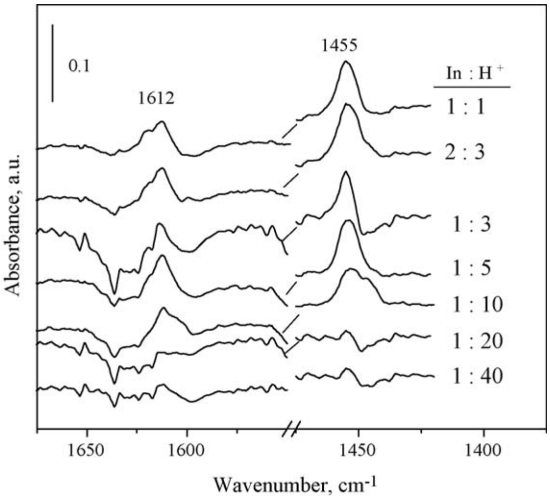

Fig. 7. Difference spectra of pyridine adsorbed on the used In,H-ZSM-5 catalysts and on the parent H-ZSM-5 zeolite. The In,H-ZSM-5 catalysts were activated in HV at 300 °C for 0.5 h, the H-ZSM-5 sample were evacuated at 400 °C for 0.5 h. After evacuation sample was contacted with pyridine at 5.7 mbar at 200 °C and degassed at 100 °C by 30-min evacuation then a spectrum was recorded at room temperature.

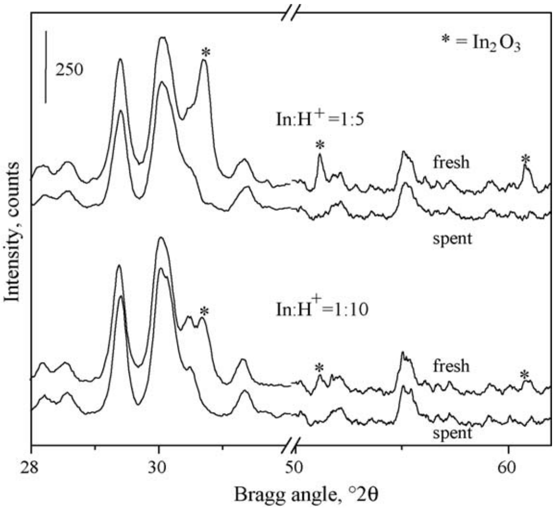

Fig. 8. XRD patterns of the mechanical In_2O_3/H-ZSM-5 (In/H^+ = 1/5 and 1/10) mixtures and the used catalysts. The reflections for In_2O_3 are marked with *.

PS data on the mechanical mixture and the used catalyst given in Table 2. The results proved that In moved from the surface into the zeolite as the concentration of In detected decreased. Note that In at exchange position can also be detected with some attenuation therefore the drop to about the half of the starting value is in line with complete exchange.

Table 2
XPS characterization of the mechanical In_2O_3/H-ZSM-5 (In/H^+ = 1/5, 1/10, 1/40) mixtures and the used catalysts.

Catalyst	In/(In + Si) (at.%)	Binding energy, In $3d_{5/2}$ (eV)
1:5		
Mixture	0.85	444.2
Used	0.43	445.6
1:10		
Mixture	0.44	444.2
Used	0.20	445.8
1:40		
Mixture	0.10	444.0
Used	0.04	446.4

The binding energy (BE) of In ($3d_{5/2}$) in the fresh In_2O_3/H-ZSM-5 mixtures appears at about 444.3 eV which is typical of the In ($3d_{5/2}$) BE in the crystalline indium(III)-oxide. Higher binding energies (about 446 eV) were observed for the used catalysts suggesting that the sample contain cationic InO^+ species. The signal at about 446 eV was ascribed to the cationic In oxo species (i.e. $(InO)^+$) [17]. Same tendency was found for In-mordenite [18] and In-ZSM-5 samples [19,20].

4. Conclusions

Starting from the mechanical mixture of In_2O_3 and H-ZSM-5, a simple method is proposed to prepare In,H-ZSM-5 catalysts for DeNOx reactions. The mixture has to be heated in inert atmosphere where In undergoes thermal auto-reduction and moves into exchange positions as In^+ without destroying the crystalline structure of the zeolite.

It was evidenced by FT-IR spectroscopy and temperature-programmed reduction and reoxidation that, once In^+ was introduced into the lattice either by reductive SSIE or thermal auto-reductive SSIE, it can be oxidized by O_2 or by the DeNOx reaction to $(InO)^+$. This oxidation step proceeds at relatively high temperature. The formed $(InO)^+$ can be reduced back to In^+. The reversible changes of the oxidation state of indium lattice cations ($In^+ \leftrightarrow (InO)^+$) makes the In,H-ZSM-5 a good candidate for catalyst in DeNOx reactions.

Selective catalytic reduction by methane proved that only a small fraction of In exchanged together with some acid sites of the zeolite form the active center for the catalytic reaction. XRD, XPS and Py FT-IR proved that the structure of the zeolite and these centers are stable under reaction conditions and In can be found mainly in the form of $(InO)^+$ in the used catalyst.

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