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# A Mechanistic Study of the Solid-State Reactions of H-Mordenite with Indium(0) and Indium(III)oxide

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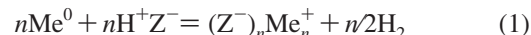
Solid-state reactions of In<sub>2</sub>O<sub>3</sub>/H-mordenite and In<sup>0</sup>/H-mordenite mixtures (Al/In = 3) were studied using an atmospheric flow-through microreactor, diffuse reflectance Fourier-transform spectroscopy (DRIFTS), and X-ray powder diffractometry (XRD). The indium(III)oxide/H-mordenite mixture was heated in a flow of 2% H<sub>2</sub>/N<sub>2</sub> gas mixture or pure N<sub>2</sub> to 873 and 973 K, respectively. The indium(0)/H-mordenite mixture was heated in a dry and wet N<sub>2</sub> stream to 673–973 K. The reactions were monitored by analyzing the effluent gas, using mass spectroscopy (MS). The protons of H-mordenite were exchanged for In<sup>+</sup> cations, indicating that In<sup>3+</sup> was reduced and In<sup>0</sup> was oxidized in the exchange processes. In the process of reductive solid-state ion exchange (RSSIE), the indium was reduced by H<sub>2</sub>. In the oxidative solid-state ion exchange (OSSIE) process, the indium was oxidized by H<sub>2</sub>O. Results substantiate that the ion exchange proceeds through a volatile InOH intermediate. Formation of InOH and its rapid transport within the zeolite crystals requires the presence of water vapor. The In<sup>+</sup> in the zeolite lattice can be oxidized by O<sub>2</sub> or H<sub>2</sub>O to indium oxyocations, most probably to InO<sup>+</sup>, while the obtained oxyocations can be reduced in hydrogen back to In<sup>+</sup>.

## 1. Introduction

Zeolites can be converted to active catalysts by simply replacing inactive exchangeable cations for active ones.<sup>1,2</sup> Conventionally, the zeolite is contacted with an aqueous solution, containing the cation to be introduced. However, this method sometimes fails. For instance, the equilibrium exchange degree can be too low, moreover, strongly acidic salt solutions cannot be used because they may damage the zeolite structure. Recently, the method of solid-state ion exchange (SSIE) attracted much attention.<sup>3–7</sup> According to the latter method, metal cations (Me<sup>n+</sup>) are introduced by simply heating a powder of a metal (Me<sup>0</sup>), metal salt, or metal oxide, finely dispersed with zeolite, in a vacuum or in a flow of inert gas. A positive feature of the SSIE method is that the equilibrium of the exchange reaction is shifted in the direction of Me-zeolite formation, if the other product of the exchange reaction is volatile. However, it may happen that the SSIE process, though thermodynamically feasible, does not proceed because of kinetic limitation, e.g., due to slow transport of the Me species within the zeolite crystals.<sup>7</sup>

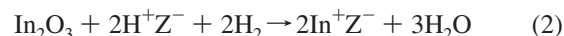
The reaction of H- or NH<sub>4</sub>-form zeolites was facile with some metals, metal halogenides, and oxides of monovalent metals, but the reaction with oxides of a two or trivalent metal was found hindered at temperatures lower than 773 K. However, the cation introduction proceeded even from latter oxides, if zeolite and metal oxide were reacted in hydrogen gas. Because the ingoing cation was reduced during the exchange, the process was referred to as reductive solid-state ion exchange (RSSIE). The introduction of ions, such as Ag, Cd, and Zn, into H-zeolites

through reaction between the metal and the zeolite was found to be both thermodynamically and kinetically feasible.<sup>7</sup> The reaction was suggested to occur according to eq 1

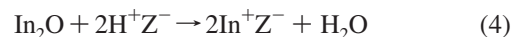
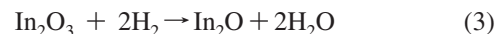


wherein Z<sup>−</sup> represents the zeolite framework and one of the negative framework charges. On the analogy of the RSSIE, this process is referred to as oxidative solid-state ion exchange (OSSIE).

The In-zeolites attract attention as active catalysts<sup>8–14</sup> and as possible precursors of microelectrical elements.<sup>15</sup> The OSSIE of In<sup>0</sup> was not examined yet, but the RSSIE of In<sub>2</sub>O<sub>3</sub> was studied in detail.<sup>16–18</sup> Different laboratories came to contradictory conclusions regarding the mechanistic details of the RSSIE process.<sup>16,19,20</sup> The first examples for RSSIE were presented by Kanazirev et al.<sup>12,16,21–24</sup> for Ga<sub>2</sub>O<sub>3</sub>/H-ZSM-5, In<sub>2</sub>O<sub>3</sub>/H-ZSM-5, and CuO/H-ZSM-5 systems. As a result of RSSIE, Me<sup>+</sup> cations were found to replace an equivalent amount of zeolite protons. The overall RSSIE reaction of In<sub>2</sub>O<sub>3</sub>/H-zeolite can be given by eq 2



According to Kanazirev et al.<sup>16</sup> the RSSIE is comprised of consecutive reduction and ion exchange steps. The In-zeolite was formed in an SSIE reaction with an In<sub>2</sub>O intermediate (eq 4), of which the intermediate was obtained by the reduction of In<sub>2</sub>O<sub>3</sub> (eq 3).



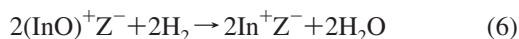
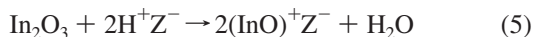
In contrast, Zhou et al.<sup>19</sup> suggested that the first step was the SSIE reaction of In<sub>2</sub>O<sub>3</sub> and H-zeolite (eq 5). In this step, InO<sup>+</sup>

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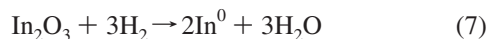
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oxycations were introduced. The In<sup>+</sup>-form zeolite was obtained in a second step, when the oxycations were reduced (eq 6).



In the absence of acidic hydroxyl groups, the In<sub>2</sub>O<sub>3</sub> was easily reduced to In<sup>0</sup> (eq 7)



suggesting that the cationic indium is more resistant to reduction if it establishes interaction with a zeolite framework.<sup>16–18</sup>

In the present work In,H-mordenite was prepared by RSSIE and OSSIE methods, and the mechanistic details of the exchange processes were examined. Results suggest that the RSSIE follows a pathway different from those outlined above. The key intermediate of both exchange processes is, most probably, volatile InOH that readily reacts with the acidic hydroxyl groups of mordenite.

## 2. Experimental

**2.1. Materials.** A zeolite NH<sub>4</sub>-mordenite (NH<sub>4</sub>-M) sample was prepared from Na-mordenite (Na-M) (Süd Chemie AG; Si/Al<sub>F</sub> = 6.7, where Al<sub>F</sub> means Al T-atom) by conventional ammonium ion exchange. The NH<sub>4</sub>-M and the Na-M were mixed with In<sub>2</sub>O<sub>3</sub> (99.99% purity, from Aldrich) applying intense grinding. The powdered mixtures, having an Al<sub>F</sub>/In ratio of 3, were then pressed into pellets; the pellets were crushed to particles; and the 0.25–0.5 mm size particle fraction was separated by sieving. This particle fraction was used in the experiments.

Following the same procedure, an In<sup>0</sup>/H-mordenite sample was prepared. The H-form mordenite (H-M) was obtained from the NH<sub>4</sub> form by thermal deammonization. The indium metal powder, obtained from Aldrich, had a purity of 99.99 wt % and was comprised of 150 μm size metal particles. The Al<sub>F</sub> to In<sup>0</sup> ratio in the physical mixture of H-mordenite and indium metal powder was 3. However, X-ray powder diffraction measurements showed that about 52% of the metal was converted to X-ray amorphous species during the intense cogrinding. The H<sub>2</sub>-TPR examination of the mixture suggested that this was an InO<sub>x</sub> species roughly having the stoichiometry of In<sub>2</sub>O (vide infra). The Al<sub>F</sub>/In<sup>0</sup> ratio of the coground mixture is, therefore, 6.25, while the Al<sub>F</sub>/In<sup>n+</sup> ratio is 5.76.

For the in situ conversion of the In<sub>2</sub>O<sub>3</sub>/NH<sub>4</sub>-M sample into the In<sub>2</sub>O<sub>3</sub>/H-M sample, a standard pretreatment procedure was applied. The sample was heated to 723 K in a 30 cm<sup>3</sup> min<sup>-1</sup> flow of 10% O<sub>2</sub>/He at a rate of 10 K min<sup>-1</sup>, kept at this temperature for 1 h, and finally, flushed with pure He while it was cooled to room temperature.

**2.2. Temperature-Programmed Reduction, Oxidation, and H<sub>2</sub> Evolution.** The measurements were carried out using a flow-through microreactor, containing about 70 mg of sample (about 45 μmol In).

The In<sub>2</sub>O<sub>3</sub>/H-M sample, obtained from the In<sub>2</sub>O<sub>3</sub>/NH<sub>4</sub>-M sample by the standard pretreatment procedure, was characterized by temperature-programmed reduction measurement, using hydrogen as the reducing gas (H<sub>2</sub>-TPR). The sample was contacted with a 30 cm<sup>3</sup> min<sup>-1</sup> flow of a 2% H<sub>2</sub>/N<sub>2</sub> mixture at room temperature. Then the reactor temperature was ramped up to 973 K at a rate of 10 K min<sup>-1</sup>. The concentrations of H<sub>2</sub> and the product H<sub>2</sub>O were continuously monitored in the effluent gas using an MS system (VG ProLab form Thermo Fisher). Data were recorded and processed by a computer. For H<sub>2</sub>

consumption and H<sub>2</sub>O formation, the MS system was calibrated by reducing a known amount of CuO under identical experimental conditions.

The sample obtained in an H<sub>2</sub>-TPR experiment (*T*<sub>max</sub> = 773 K) was characterized by temperature-programmed oxidation measurement (O<sub>2</sub>-TPO). The experimental conditions were the same as those at H<sub>2</sub>-TPR, except that a 10% O<sub>2</sub>/He mixture was used and the O<sub>2</sub> concentration was monitored in the effluent.

The In<sup>0</sup>/H-M mixture was heated up in 30 cm<sup>3</sup> min<sup>-1</sup> N<sub>2</sub> flow without pretreatment, and the concentration of the evolved H<sub>2</sub> was monitored in the effluent gas. This experiment, referred to as temperature-programmed H<sub>2</sub> evolution (TPHE), was also carried out with wet N<sub>2</sub> flow (0.6% H<sub>2</sub>O/N<sub>2</sub>), of which the flow was prepared by saturating the N<sub>2</sub> flow with water at 273 K.

Because H<sub>2</sub> evolution and In oxidation are conjunct processes, TPHE can be considered as a kind of TPO.

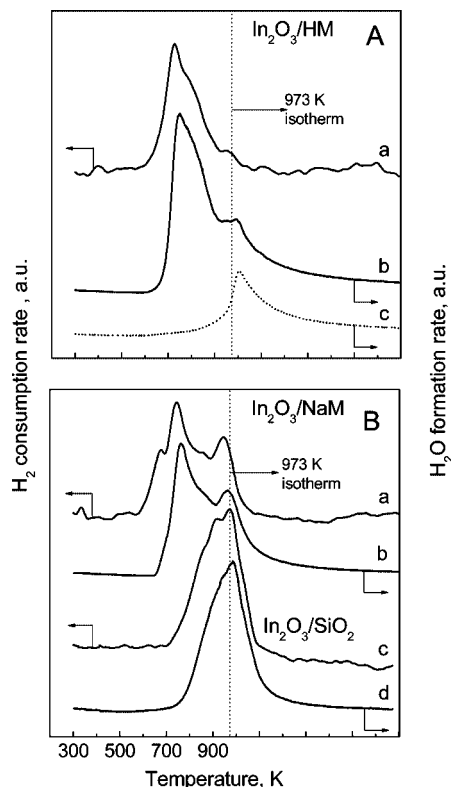
**2.3. DRIFT Spectroscopic Investigations.** *Operando* H<sub>2</sub>-TPR/DRIFT spectroscopic investigation was carried out by placing a powdered sample (~12 mg) into a high-temperature/high-pressure DRIFTS reactor cell (Spectra-Tech, Inc.). In a 15 cm<sup>3</sup> min<sup>-1</sup> flow of a 2% H<sub>2</sub>/N<sub>2</sub> gas mixture, the sample was heated at a rate of 10 K min<sup>-1</sup> to 873 K. DRIFT spectra of the solid were recorded in 2.5 min intervals, while the effluent gas from the DRIFTS reactor cell was analyzed by MS as above. The same DRIFTS cell was used for additional in situ spectroscopic examinations of the samples.

**2.4. XRD Measurements.** A Philips PW 1810/1870 diffractometer, equipped with an Anton Parr chamber, Ni filter, and Cu K<sub>α</sub> X-ray source, was used. Treatments of In<sub>2</sub>O<sub>3</sub>/HM, In<sub>2</sub>O<sub>3</sub>/NaM, and In<sup>0</sup>/HM samples were carried out in situ in a controlled gas atmosphere at elevated temperatures. The XRD pattern of the samples was recorded at room temperature.

## 3. Results

**3.1. Temperature-Programmed Reduction of In<sub>2</sub>O<sub>3</sub>/Mordenite Mixtures.** H<sub>2</sub>-TPR curves of In<sub>2</sub>O<sub>3</sub>/H-M and In<sub>2</sub>O<sub>3</sub>/Na-M and In<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> mixtures are shown in Figure 1. The curves represent the H<sub>2</sub> consumption rate and the formation rate of reduction product H<sub>2</sub>O. Water release begins at temperatures about 50 K higher than the starting temperature of H<sub>2</sub> consumption. The strong adsorption of water in the zeolite pores explains this delayed desorption. Nevertheless, the shapes of the corresponding H<sub>2</sub> consumption and H<sub>2</sub>O formation curves are quite similar, with the exception of the water desorption peak above 973 K on the pattern of the In<sub>2</sub>O<sub>3</sub>/H-M sample, for which the water-release peak does not have a corresponding H<sub>2</sub> consumption peak (Figure 1A, a, b). A similar water desorption peak was obtained when a pure H-M sample was used in an identical experiment (Figure 1A, dotted line). Results suggest that the high-temperature water evolution is related with H-zeolite dehydroxylation. It is important to note that reduction of the In<sub>2</sub>O<sub>3</sub>/mordenite mixtures starts at about 623 K, regardless of the cationic form of the mordenite component (Figure 1A, a and 1B, a), while the starting temperature of reduction is about 80 K higher, when the support is a low surface area SiO<sub>2</sub> (Figure 1B, c). It is also worth mentioning that the mixture containing H-M remained white, while the one containing Na-M or SiO<sub>2</sub> became slightly gray upon reduction.

The H/In and H<sub>2</sub>O/In molar ratios calculated from the total amount of H<sub>2</sub> consumed and H<sub>2</sub>O formed, respectively, during the reduction process are given in Table 1. The amount of water obtained from the In<sub>2</sub>O<sub>3</sub>/H-M sample was corrected with the amount of water, which was possibly formed due to thermal dehydroxylation. (The made correction was two-thirds of the



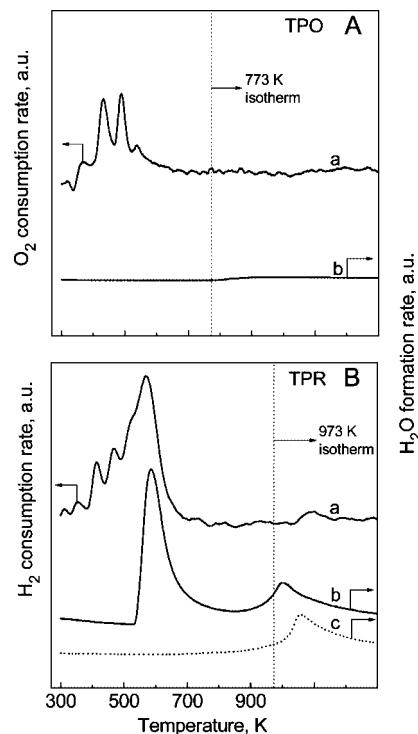
**Figure 1.**  $\text{H}_2$ -TPR curves measured on (A)  $\text{In}_2\text{O}_3/\text{H-M}$  and (B)  $\text{In}_2\text{O}_3/\text{Na-M}$  and  $\text{In}_2\text{O}_3/\text{SiO}_2$ . Solid lines (a) and (c):  $\text{H}_2$  consumption rate. (b) and (d): formation rate of  $\text{H}_2\text{O}$  in the function of temperature. Dotted line (c) was measured on H-M under identical conditions. The  $\text{In}_2\text{O}_3/\text{H-M}$  sample was prepared in situ in a flow-through microreactor by treating the  $\text{In}_2\text{O}_3/\text{NH}_4\text{-M}$  mixture ( $\text{Al}/\text{In} = 3$ ) in 10%  $\text{O}_2/\text{He}$  at 723 K for 1 h, cooling the sample in pure He flow to room temperature. The obtained  $\text{In}_2\text{O}_3/\text{H-M}$  sample was heated up in a  $30 \text{ cm}^3$  (STP)  $\text{min}^{-1}$  flow of 2%  $\text{H}_2/\text{N}_2$  gas at a rate of  $10 \text{ K min}^{-1}$  to 973 K, at which the temperature was maintained. The  $\text{H}_2$  and the  $\text{H}_2\text{O}$  concentration of the reactor effluent were monitored by MS.

**TABLE 1: H/In and  $\text{H}_2\text{O}/\text{In}$  Ratios Obtained from  $\text{H}_2$ -TPR Measurements**

sample	H/In	$\text{H}_2\text{O}/\text{In}$
$\text{In}_2\text{O}_3/\text{H-M}$	1.97 <sup>a</sup>	1.53 <sup>a,b</sup>
$\text{In}_2\text{O}_3/\text{Na-M}$	2.95 <sup>a</sup>	1.70 <sup>a</sup>
$\text{In}_2\text{O}_3/\text{SiO}_2$	3.0 <sup>a</sup>	1.50 <sup>a</sup>
In,H-M <sup>c</sup>	1.88 <sup>d</sup>	0.91 <sup>d</sup>

<sup>a</sup> Calculated from the results shown in Figure 1. For measurement conditions, see the legend of Figure 1. <sup>b</sup> Correction was made for the  $\text{H}_2\text{O}$  release due to thermal dehydroxylation. <sup>c</sup> Carried out after  $\text{O}_2$ -TPO measurement on the In,H-M sample prepared by RSSIE. <sup>d</sup> Calculated from the results shown in Figure 2B. For measurement conditions, see the legend of Figure 2.

amount of water evolved from H-M under identical conditions; i.e., the correction was proportional with the hydroxyl concentration of the In-exchanged sample.) Both the H/In and  $\text{H}_2\text{O}/\text{In}$  values determined for the  $\text{In}_2\text{O}_3/\text{H-M}$  sample are close to the stoichiometric values of 2.0 and 1.5 according to eq 2. For the reduction of the  $\text{In}_2\text{O}_3/\text{Na-M}$  sample, the stoichiometric values according to eq 7 are  $\text{H}/\text{In} = 3.0$  and  $\text{H}_2\text{O}/\text{In} = 1.5$ . The latter values show also good correspondence with those measured. The reduction stoichiometry of the  $\text{In}_2\text{O}_3/\text{SiO}_2$  mixture was about the same as that of the  $\text{In}_2\text{O}_3/\text{Na-M}$  mixture; however, its  $\text{H}_2$ -TPR pattern was somewhat different (Figure 1B, c,d). The  $\text{H}_2$  consumption and the  $\text{H}_2\text{O}$  formation were virtually concurrent,



**Figure 2.** Curves of (A)  $\text{O}_2$ -TPO and (B)  $\text{H}_2$ -TPR for the In,H-M sample prepared by the RSSIE method. Curves (a) and (b) represent rates of (A)  $\text{O}_2$ , (B)  $\text{H}_2$  consumption, and  $\text{H}_2\text{O}$  formation, respectively. To get the In,H-M sample, an  $\text{In}_2\text{O}_3/\text{H-M}$  mixture, prepared in situ as described in the legend of Figure 1, was heated in a flow of  $30 \text{ cm}^3$  (STP)  $\text{min}^{-1}$  2%  $\text{H}_2/\text{N}_2$  gas to 773 K at a rate of  $10 \text{ K min}^{-1}$  and kept in the gas flow at this temperature for 1 h and then cooled to room temperature in a pure He flow. The (A)  $\text{O}_2$ -TPO curves were determined by heating the In,H-M sample in 10%  $\text{O}_2/\text{He}$  at a rate of  $10 \text{ K min}^{-1}$  up to 773 K, at which the temperature was maintained. The isothermal part is right of the dotted vertical line. The  $\text{O}_2$  and the  $\text{H}_2\text{O}$  concentrations of the reactor effluent were monitored by MS. After the  $\text{O}_2$ -TPO measurement sample was flushed with He and (B), an  $\text{H}_2$ -TPR measurement was carried out the same way as is described in the legend of Figure 1. The dotted curve (c) in Figure 2B was recorded for zeolite H-M.

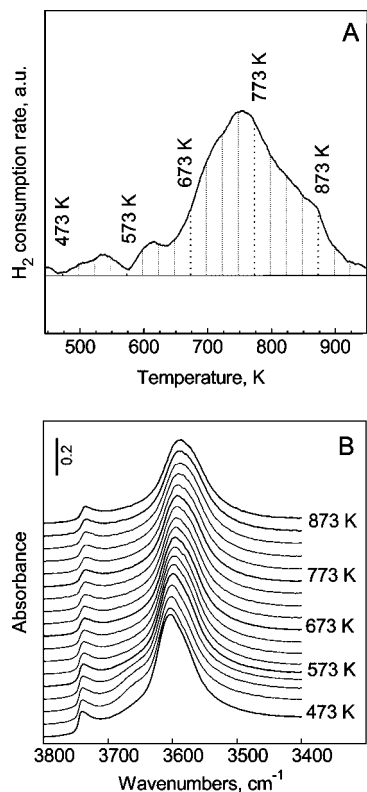
indicating that the silica released the product  $\text{H}_2\text{O}$  more rapidly than the zeolite.

The above results infer that zeolite hydroxyl groups do not play any role in the  $\text{H}_2$ -consuming first step of the RSSIE process. The second step is the stabilization of the indium cations in a reaction between the indium species, formed in the first step, and the H-mordenite. In the absence of acidic hydroxyl groups, the second step cannot occur. The  $\text{H}_2$  consuming process continues until  $\text{In}^0$  is obtained.

According to the  $\text{O}_2$ -TPO curve, shown in Figure 2A, reoxidation of the In,H-mordenite, obtained by the above outlined RSSIE method, starts below 373 K. The reduction in a subsequent  $\text{H}_2$ -TPR experiment also starts well below 373 K (Figure 2B) and reaches a maximum rate at about 573 K. This characteristic temperature is more than 100 K lower than that of the  $\text{In}_2\text{O}_3/\text{H-M}$  reduction (Figure 1A). The H/In and  $\text{H}_2\text{O}/\text{In}$  values suggest that the number of O-atoms participating in the redox process is equal with the number of In atoms in the In,H-mordenite (Table 1).

**3.2. Reductive and Autoreductive Solid-State Ion Exchange (RSSIE and ARSSIE) of  $\text{In}_2\text{O}_3/\text{H-mordenite}$ .** The extent of  $\text{H}_2$  consumption and zeolite dehydroxylation was simultaneously recorded by combining the potentials of the  $\text{H}_2$ -TPR/MS and the *operando* DRIFTS methods (Figure 3). The



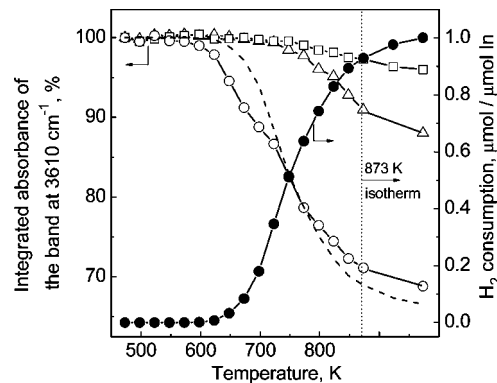


**Figure 3.** Results of *operando* H<sub>2</sub>-TPR/DRIFTS/MS measurement. (A) H<sub>2</sub>-TPR curve obtained from the In<sub>2</sub>O<sub>3</sub>/H-M mixture and (B) the DRIFT spectra of the  $\nu_{\text{OH}}$  region collected at the indicated temperatures. The measurement was carried out as described in the legend of Figure 1 using a flow-through high-temperature DRIFTS cell as a microreactor.

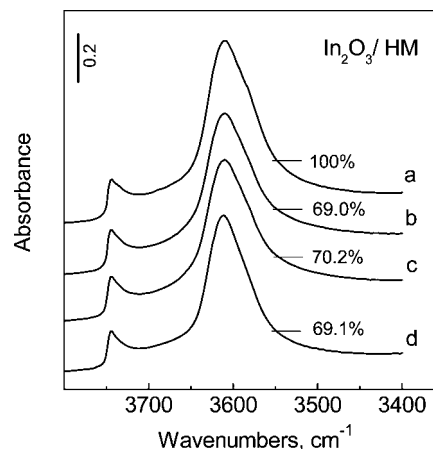
reduction of the In<sub>2</sub>O<sub>3</sub>/H-M sample began at around 623 K (Figure 3A) resulting in a concomitant decrease of the integrated absorbance of the  $\nu_{\text{OH}}$  band of H-mordenite at 3610 cm<sup>-1</sup> (Figure 3B). The corresponding H<sub>2</sub> consumption and integrated absorbance values as a function of reduction temperature are also shown in Figure 4 (*vide infra*). Results clearly show that the Brønsted acid hydroxyl groups of the zeolite are involved in the process according to eq 2. In the absence of H<sub>2</sub> in the gas flow, no dehydroxylation occurred below 773 K (Figure 4). Thus, the RSSIE fully accounts for the zeolite dehydroxylation up to about this temperature. At the end of the reduction experiment, the total intensity loss of the OH band was 31.2% (Figure 4), which is close to the 33% corresponding to the In/Al<sub>F</sub> ratio of the sample and the stoichiometry of eq 2.

The In,H-mordenite sample obtained by RSSIE can be oxidized by O<sub>2</sub> and reduced by H<sub>2</sub> (*vide supra* in Figure 2). Figure 5 shows that changing the oxidation state of the indium did not affect the zeolite OH-band.

The H<sub>2</sub> consumption, expressed as H<sub>2</sub>/In, and the intensity of the  $\nu_{\text{OH}}$  band, normalized to the initial band intensity, were plotted against the temperature (Figure 4). The dotted line in Figure 4 represents the intensity of the OH-band, calculated from the H<sub>2</sub> consumption assuming the stoichiometry of eq 2. The calculated and experimental curves fairly overlap above about 673 K. Below this temperature, the normalized band intensity underestimates the real hydroxyl concentration of the sample. The reason is that some of the water, obtained from the reduction of In<sub>2</sub>O<sub>3</sub>, remains H-bound to the acidic OH-groups. The hydroxyl groups and H-bonding water give broad bands at around 2900, 2400, and 1700 cm<sup>-1</sup> (not shown), known as an



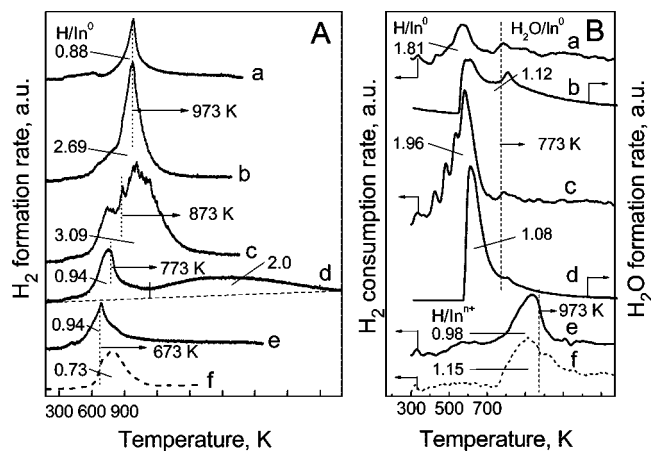
**Figure 4.** *Operando* H<sub>2</sub>-TPR/DRIFTS/MS characterization of the RSSIE and ARSSIE processes. The H<sub>2</sub> consumption (full circles) and the extents of dehydroxylation (open circles) are shown as a function of the temperature for the In<sub>2</sub>O<sub>3</sub>/H-M sample. The dashed line gives the extent of dehydroxylation calculated from the H<sub>2</sub> consumption using eq 2. The dehydroxylation of the In<sub>2</sub>O<sub>3</sub>/H-M mixture (open triangles) and the thermal dehydroxylation of the H-M sample (open squares) in N<sub>2</sub> flow are also given. To get the extent of dehydroxylation at different temperatures, the integrated absorbances of the  $\nu_{\text{OH}}$  band of bridged hydroxyl groups was related to the integrated absorbance of the band measured at 473 K. The experimental conditions are the same as given in the legends of Figures 1 and 3.



**Figure 5.** DRIFT spectra of the  $\nu_{\text{OH}}$  region of samples, obtained from the In<sub>2</sub>O<sub>3</sub>/NH<sub>4</sub>-M mixture by the following subsequent treatments: (a) 10% O<sub>2</sub>/He flow at 723 K for 1 h, (b) pure H<sub>2</sub> flow at 773 K for 1 h, (c) 10% O<sub>2</sub>/He flow at 673 K for 1 h, and (d) 2% H<sub>2</sub>/N<sub>2</sub> flow at 773 K for 1 h. After each treatment, the sample was cooled to room temperature in pure He flow, and the spectrum was recorded. Treatments provide (a) In<sub>2</sub>O<sub>3</sub>/H-M sample, (b) In,H-M product of RSSIE, (c) 2e oxidation, and (d) 2e reduction of the In,H-M sample. The integrated absorbance of the bands was related to that of band (a) and is given in percent.

ABC triad.<sup>25</sup> The latter bands practically disappeared over about 673 K, where the amount of retained water became negligible.

In a flow of inert gas, the exchange of the zeolite protons for cationic indium species proceeds to some extent at temperatures higher than 773 K. This is evident if the decrease of zeolite OH concentration is compared in the presence and absence of In<sub>2</sub>O<sub>3</sub> (Figure 4). The intensity (integrated absorbance) of the 3610-cm<sup>-1</sup> band of H-M decreased less than 5%, while that of In<sub>2</sub>O<sub>3</sub>/H-M dropped about 12%. Thus, at least 7% of the OH groups must have participated in the exchange. The exchange was paralleled by simultaneous O<sub>2</sub> and H<sub>2</sub>O formation, showing that autoreduction of In<sub>2</sub>O<sub>3</sub> has significance in the generation of the ingoing indium species. This process was referred to as the autoreductive solid-state ion exchange (ARSSIE) process.<sup>26</sup>

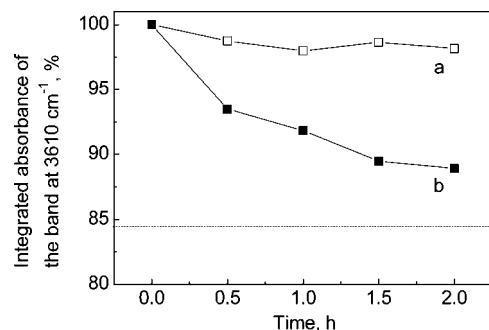


**Figure 6.** (A) Curves of temperature-programmed H<sub>2</sub>-evolution of the In<sup>0</sup>/H-M mixture (Al/In = 3). The mixture was heated in a 30 cm<sup>3</sup> (STP) min<sup>-1</sup> flow of (a) N<sub>2</sub> or (b)–(e) 0.6% H<sub>2</sub>O/N<sub>2</sub> gas to the temperature, indicated by the dotted vertical line that was maintained until the curve returned to the baseline. Curve (f) was obtained for the In<sup>0</sup>/SiO<sub>2</sub> mixture. (B) Rates of H<sub>2</sub> consumption and H<sub>2</sub>O formation in H<sub>2</sub>-TPR measurements using the samples obtained in the experiments of section A(d) and section A(e). The TPR curves of (a,b,c,d) refer to the sample from experiment A(d), and the TPR curve of (e) refers to the sample from experiment A(e). Curves (c) and (d) were obtained using the sample, obtained in the H<sub>2</sub>-TPR measurement of section B(a,b) after reoxidation in 10% O<sub>2</sub>/He flow at 773 K. Curve (f) was obtained using the starting In<sup>0</sup>/H-M mixture (containing both In<sup>0</sup> and InO<sub>x</sub> species) without any pretreatment. For H<sub>2</sub>-TPR conditions, see the legend of Figure 1. The H<sub>2</sub> evolutions and consumptions were related to the In<sup>0</sup> and In<sup>III</sup> fraction, respectively, of the total indium content of the In<sup>0</sup>/H-M mixture.

### 3.3. Oxidative Solid-State Ion Exchange (OSSIE) of the In<sup>0</sup>/H-M Mixture.

To learn about the mechanistic details of the solid-state reaction between In<sup>0</sup> and H-M, TPHE experiments were carried out using dry and wet nitrogen as the carrier gas (Figure 6, a). In dry N<sub>2</sub>, some hydrogen release was observed between 373 and 673 K and rapid H<sub>2</sub> evolution above 773 K (Figure 6A). Notice that the high-temperature (HT) H<sub>2</sub> evolution took place in the same temperature region where the dehydroxylation of the zeolite occurred (Figure 1A, c). Water is able to oxidize In<sup>0</sup> at elevated temperature even in the absence of strong acid support. This was evidenced by the TPHE curve of an In/SiO<sub>2</sub> mixture using a wet N<sub>2</sub> stream, containing 0.6% water vapor (Figure 6A, f). In a dry N<sub>2</sub> stream, adsorbed water could induce low-temperature (LT) hydrogen evolution. Also, the water, formed by dehydroxylation, could effect the rapid HT H<sub>2</sub> generation.

In wet N<sub>2</sub>, the hydrogen evolution started at a lower temperature than in the dry gas and was more pronounced (Figure 6A, b). In an attempt to separate LT and HT peaks, TPHE curves of the In<sup>0</sup>/H-M mixture were recorded using different heating programs. The programs differed in the temperature where the temperature raising was stopped and maintained until the H<sub>2</sub> evolution was finished, i.e., until the TPHE curve returned to the baseline. Figure 6A, c clearly shows that two processes can be distinguished. The first process starts at around 573 K. The second process continues at the maintained 873 K. When the temperature of the isothermal region of the TPHE experiment was 773 K, perfectly separated LT and HT peaks were obtained (Figure 6A, d). The HT H<sub>2</sub> evolution was slower as indicated by the broader peak. When the temperature was not raised above 673 K, the second H<sub>2</sub> evolution process already did not occur (Figure 6A, e). The amount of the evolved H<sub>2</sub> was about twice as much in the HT than in the LT process



**Figure 7.** Integrated absorbance of the ν<sub>OH</sub> band of (a) H-M and (b) In<sup>0</sup>/H-M as a function of time on a 30 cm<sup>3</sup> (STP) min<sup>-1</sup> stream of 0.6% H<sub>2</sub>O/N<sub>2</sub> at 773 K. The dotted line indicates the OH-loss equivalent with the In<sup>0</sup> content of the sample.

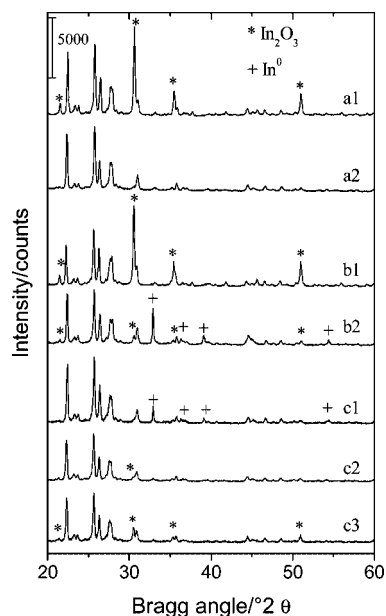
(Figure 6A, d). The H/In<sup>0</sup> values, given in Figure 6A, were obtained by relating the molar amount of evolved hydrogen to the molar amount of indium that was In<sup>0</sup> at the beginning of the experiment; i.e., the indium of the InO<sub>x</sub> species generated during cogrinding the In<sup>0</sup>/HM mixture was disregarded. At an average, the H<sub>2</sub> amounts correspond to about 1e and 2e oxidation processes at LT and HT, respectively.

The H<sub>2</sub>-TPR of the InO<sub>x</sub> species generated during cogrinding the In<sup>0</sup>/HM mixture is shown in Figure 6B, f. Each cationic indium suffered an about 1e reduction in the temperature range of 773–973 K. The H<sub>2</sub>-TPR curves of the samples obtained in the experiments of Figure 6A, d and Figure 6A, e are shown in Figure 6B, a and Figure 6B, e, respectively. The H<sub>2</sub> uptakes are expressed as H/In<sup>0</sup>; i.e., the hard-to-reduce InO<sub>x</sub> was considered as a species that does not consume hydrogen in the temperature range of the experiment at all. The H<sub>2</sub> consumption and H<sub>2</sub>O formation curves (Figure 6B, a, b) resemble the H<sub>2</sub>-TPR curves obtained for the In,H-mordenite sample, prepared by the RSSIE method (cf. Figure 2B and 6B). Due to possible thermal dehydroxylation (cf. Figure 1 and Table 1), somewhat more H<sub>2</sub>O was formed than that, equivalent with the consumed H<sub>2</sub> (Figure 6B, a, b). The hydrogen consumption, H/In<sup>0</sup> = 1.81 (Figure 6B, a), was close to the amount of H<sub>2</sub> evolution at 773 K in wet nitrogen flow (H/In<sup>0</sup> = 2.0, Figure 6A, d).

The ν<sub>OH</sub> band was monitored by in situ DRIFT spectroscopy, while the H-M or the In<sup>0</sup>/H-M mixture was contacted by wet N<sub>2</sub> flow at 773 K for 2 h. Under the same conditions, the dehydroxylation of the H-M was negligible (Figure 7, a). In contrast, the hydroxyl concentration of the In<sup>0</sup>/H-M decreased by about 12% (Figure 7, b). The observed 12% decrease suggests that nearly all In<sup>0</sup> participated in the OSSIE process. A 16% dehydroxylation could be reached if each of the In<sup>0</sup> atoms eliminated one hydroxyl group (Figure 7, dotted line). After 2 h, the wet N<sub>2</sub> flow was changed for dry H<sub>2</sub> flow. Hydrogen was consumed (vide infra), but the ν<sub>OH</sub> band was not affected at all.

Above results infer that the H<sub>2</sub> reduction reversed the change of oxidation state caused by the HT water treatment of the sample. The treatment using wet N<sub>2</sub> must have generated cationic indium species. This cationic species carry extra-framework oxygen (EFO), which is removed when the sample is reduced by H<sub>2</sub>. Since reduction left the hydroxyl concentration unchanged, reduction could not vary the average net charge of the cationic In species. The sample, reoxidized according to the standard treatment in O<sub>2</sub>/He flow, showed similar H<sub>2</sub>-TPR characteristics than the reoxidized RSSIE sample (cf. Figure 6B, c,d and Figure 2B, a,b).

The sample, obtained from the reaction of the In<sup>0</sup>/H-M mixture with wet N<sub>2</sub> at 673 K, did not consume H<sub>2</sub> below 773



**Figure 8.** XRD patterns of (a1)  $\text{In}_2\text{O}_3/\text{H-M}$ , (b1)  $\text{In}_2\text{O}_3/\text{Na-M}$  ( $\text{Al}/\text{In} = 3$ ), and (c1)  $\text{In}^0/\text{H-M}$  ( $\text{Al}/\text{In} = 3$ ) mixtures. Patterns (a2) and (b2) were recorded after treating the corresponding mixture in  $\text{H}_2$  flow at 773 K for 1 h. Patterns (c2) and (c3) were determined for the samples obtained from the experiments of Figure 6A, e (0.6%  $\text{H}_2\text{O}/\text{N}_2$  at 673 K) and Figure 6A, d (0.6%  $\text{H}_2\text{O}/\text{N}_2$  at 773 K), respectively. Measurements were carried out at room temperature.

K (Figure 6B, e). This result can indicate that  $\text{In}^+$  was introduced into the zeolite, but it was not oxidized to EFO-carrying  $\text{In}^{3+}$ . The  $\text{H}_2$  consumption above 773 K comes most probably from the reduction of  $\text{InO}_x$  species.

**3.4. XRD Examination of the Reductive and Oxidative Solid-State Ion Exchange (RSSIE and OSSIE).** The reaction of  $\text{In}_2\text{O}_3$  and H-mordenite in  $\text{H}_2$  flow at 773 K results in complete disappearance of the  $\text{In}_2\text{O}_3$  XRD reflections (Figures 8, a1 and a2). The relative XRD intensities of the mordenite reflections slightly changed. Formation of a new crystalline phase could not be discerned. Results are in correspondence with that expected if RSSIE takes place. The absence of the  $\text{In}^0$  phase suggests that the zeolite stabilized the indium as a cationic species.

The XRD patterns of the  $\text{In}_2\text{O}_3/\text{Na-M}$  and the  $\text{H}_2$ -reduced  $\text{In}_2\text{O}_3/\text{Na-M}$  samples are shown in Figures 8, b1 and b2, respectively. Because indium melt, the expected product at the reduction temperature (the mp of indium metal is 430 K), does not give XRD reflection, the measurements were made at room temperature, where the indium metal can form a solid crystalline phase. The intensity loss of the  $\text{In}_2\text{O}_3$  reflections was accompanied by the appearance of reflections from  $\text{In}^0$ . The average particle size of  $\text{In}_2\text{O}_3$  in the mechanical mixture was  $\sim 0.2 \mu\text{m}$  as estimated by the Debye-Scherrer method. After reduction at 823 K, the average size of the  $\text{In}^0$  particles was about  $1 \mu\text{m}$ . The XRD examination suggests that, in agreement with the results of the  $\text{H}_2$ -TPR measurements, reduction of the  $\text{In}_2\text{O}_3/\text{Na-M}$  mixture gives  $\text{In}^0$  according to eq 7. Thus, the Na-M cannot stabilize cationic indium. The reduction proceeds until indium(0) is formed.

The XRD pattern of the  $\text{In}^0/\text{H-M}$  mixture was recorded without any treatment (Figure 8, c1) and after the TPHE experiments of Figures 6A, e and 6A, d (Figure 8, c2 and c3). The  $\text{In}^0$  reflections were about half as intense as those obtained for the reduced  $\text{In}_2\text{O}_3/\text{Na-M}$  mixture (cf. Figure 8, b2 and c1). This is surprising, because the two samples contain the same

amount of indium. In the XRD pattern of the coground  $\text{In}^0/\text{H-M}$  mixture, no phase could be detected other than  $\text{In}^0$  and H-M; however,  $\text{H}_2$ -TPR results evidenced the formation of an X-ray amorphous  $\text{InO}_x$  species. The oxidation of the  $\text{In}^0$  metal must have been effected by the intense cogrinding of the mixture. The mechanochemical indium oxidation is an example for the mechanochemical transformations, extensively discussed in the literature.<sup>27</sup> The fraction of  $\text{In}^0$  that avoided mechanochemical oxidation was estimated by relating the intensities of the  $\text{In}^0$  reflections in Figures 8, c1 and 8, b2.

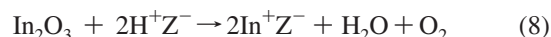
The absence of  $\text{In}^0$  reflections in the XRD patterns of the samples treated by wet  $\text{N}_2$  up to 673 K suggests that all the  $\text{In}^0$  became oxidized (Figure 8, c2). The relative intensity of the mordenite reflections changed, indicating that cationic indium species could take some of the lattice positions. A detectable amount of  $\text{In}_2\text{O}_3$  was found in the sample wherein each  $\text{In}^0$  that avoided mechanochemical oxidation was oxidized by near to 3e (Figure 6A, d and 8, c3).

The above results support the notation that water vapor effected indium oxidation and promoted the exchange reaction between the oxidized In species and the H-mordenite.

#### 4. Discussion

The most interesting mechanistic question, regarding the incorporation of indium into the zeolite lattice from solid  $\text{In}_2\text{O}_3$  or  $\text{In}^0$ , concerns the specification of the In species, which is able to rapidly move in narrow channels to hidden zeolite cages and react there with acidic hydroxyl groups.

At temperatures below 750–800 K, where the RSSIE process results in deep exchange, the SSIE reaction of  $\text{In}_2\text{O}_3$  and H-zeolites<sup>17–19</sup> does not proceed at all (Figure 4). This finding excludes that the RSSIE mechanism, expressed by eqs 5 and 6, could operate. However, some exchange occurred even in inert gas or vacuum at temperatures between 773 and 873 K. It was shown that the latter process was fully inhibited by a minor amount of  $\text{O}_2$ , strongly evidencing that the  $\text{In}_2\text{O}_3$  component became autoreduced by  $\text{O}_2$  release prior to the SSIE reaction. It has also been shown that nearly complete exchange occurs only at 973 K in air flow.<sup>20</sup> The auto reduction and the solid-state exchange, i.e., the ARSSIE can be described by eq 8<sup>26</sup>



The RSSIE was assumed to proceed similarly, but because of the more facile reduction of  $\text{In}_2\text{O}_3$  in hydrogen, the reaction comes rapidly to an end at much lower temperature (eq 2).

It was suggested that the reaction proceeds through intermediate indium(I)oxide formed according to eq 3, which reacts then with zeolite hydroxyl groups (eq 4).<sup>16</sup> As an alternative mechanism, we considered that the reduction of  $\text{In}_2\text{O}_3$  might go to  $\text{In}^0$  first, which could be oxidized then by the zeolite protons according to eq 1. As a matter of fact, neither  $\text{In}_2\text{O}$  nor  $\text{In}^0$  could be detected by XRD as a reaction intermediate under the conditions of the RSSIE or ARSSIE reactions of the  $\text{In}_2\text{O}_3/\text{H-M}$  mixture. Under conditions of ARSSIE, when  $\text{N}_2$  is used as carrier gas,  $\text{H}_2$  formation could be detected, if  $\text{In}^0$  was the intermediate of the process. However,  $\text{O}_2$  and  $\text{H}_2\text{O}$  were the only products that appeared in the  $\text{N}_2$  stream. The  $\text{O}_2$  formation evidenced the auto reduction, but based only on the absence of  $\text{H}_2$ , the formation of intermediate  $\text{In}^0$  cannot be excluded. The  $\text{H}_2$ , if formed, could react with  $\text{O}_2$  to give  $\text{H}_2\text{O}$ . In the latter reaction, the same amount of water can be obtained as in the exchange between the H-zeolite and, e.g.,  $\text{In}_2\text{O}$ . Nevertheless, considering the low vapor pressure, neither  $\text{In}_2\text{O}$  nor  $\text{In}^0$  seems to be the intermediate of the RSSIE or ARSSIE processes. The

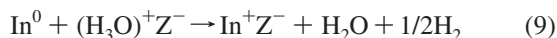


vapor pressure of In<sub>2</sub>O at 923–973 K is as low as 10<sup>-2</sup>–10<sup>-3</sup> Pa.<sup>28</sup> Thus, at the much lower temperature of the RSSIE reaction, the concentration of the In<sub>2</sub>O in the gas phase must be too low to explain the observed rapid exchange (Figure 1). Incorporation of metal cations via oxidation of metal atoms by zeolite protons has been observed for metals, having negative standard redox potential, e.g., Zn<sup>0</sup> or Cd<sup>0</sup>,<sup>6,7</sup> at relatively low temperatures (<800 K). However, the vapor pressure of these metals at the temperature of the reaction is about 30–100 kPa, much higher than that of In<sup>0</sup> (8 × 10<sup>-6</sup> Pa at 800 K). The found rapid exchange reaction presumes fast transport of the reacting indium species in the zeolite pores. It is very unlikely that this species could be the In<sup>0</sup> because of the low vapor pressure of the metal.

A salient finding of the present work is that incorporation of cationic indium species from indium(0) or indium(III)oxide occurs by the increase or the decrease of the oxidation state, respectively, and that it always proceeds in the presence of water vapor. The results, shown in Figure 6, do not substantiate that OSSIE of In<sup>0</sup> could take place according to eq 1 because significant H<sub>2</sub> evolution was obtained in the presence of water vapor only. When dry nitrogen was used as carrier gas, the H<sub>2</sub> evolution was detected at the temperatures where zeolite-bound water desorbed and at the temperature where zeolite dehydroxylation was already significant. Similarly, the ARSSIE took place at the temperature of thermal zeolite dehydroxylation. The water, regardless of its origin, can initiate the ion-exchange process that can provide additional water (Figure 4). The presence of H<sub>2</sub> in the RSSIE facilitates the change of oxidation state and simultaneously provides water to promote the exchange process.

The above results suggest that water participates in the formation of an In compound, which can easily penetrate into the pores. The most probable intermediate is InOH. The indium(I)hydroxide is a volatile species. The reaction of the InOH and the zeolite hydroxyl groups is a facile acid–base reaction, giving In,H-zeolite and water.

The formation of InOH has been unambiguously detected in the reaction of metallic In<sup>0</sup> and water vapor or between H<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>.<sup>29,30</sup> Thus, the overall OSSIE reaction can be written as the dissolution reaction of In<sup>0</sup> in a strong acid. The results, shown in Figure 6, suggest that water oxidizes the indium in two steps: first to InOH, which is the substantiated intermediate of the exchange. The gross process of In<sup>0</sup> oxidation and In<sup>+</sup> exchange into the zeolite is given by eq 9.



As a side reaction, In<sup>0</sup> can be converted to In(OH)<sub>3</sub> or InO(OH), and species may not react with the zeolite hydroxyl groups but are reduced in the H<sub>2</sub>-TPR process as suggested by the appearance of the HT side peaks of the main reduction peak (Figure 6B, a)

The InOH formation from In<sub>2</sub>O<sub>3</sub> must be introduced by reduction of the In<sup>3+</sup> to In<sup>+</sup> or In<sup>0</sup>. If In<sup>0</sup> was the reduction product, then the exchange could continue according to eq 9. However, as discussed above, no H<sub>2</sub> could be detected during ARSSIE. This is substantiating that the InOH intermediate of the ARSSIE is formed in the reaction

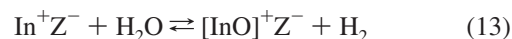


In the RSSIE, the presence of H<sub>2</sub> facilitates the reduction of In<sup>3+</sup> and the InOH formation.



In lack of excess water, the primary product of the RSSIE is In,H-zeolite, containing In<sup>+</sup> cations.<sup>16–18</sup> These cations can be

easily oxidized either with O<sub>2</sub> or with H<sub>2</sub>O to In<sup>3+</sup> species carrying extra-framework oxygen, such as [InO]<sup>+</sup> (eqs 12 and 13)<sup>17,18</sup>



The redox processes given by eqs 12 and 13 do not change the net charge on the indium species. This is in accordance with the finding that reduction or oxidation of the In-mordenite did not change the OH concentration of the zeolite.

If the acidic support of indium was richer in hydroxyl groups than the H-mordenite, such as the H-Y<sup>17</sup> or material MCM-41,<sup>31</sup> further reactions were found to proceed that can include the formation of polyoxycations or can bring about the exchange by multivalent cationic indium species charge balanced only by framework oxygen atoms.

## 5. Conclusions

Indium can be introduced into zeolites as an exchange cation by reacting the H-form of the zeolite and In<sup>0</sup> or In<sub>2</sub>O<sub>3</sub> in the solid state. The exchange proceeds most probably via volatile InOH intermediate. The InOH is formed at elevated temperature by the dissolution of In<sup>0</sup> in H<sub>2</sub>O or by reaction of In<sub>2</sub>O, formed by autoreduction from In<sub>2</sub>O<sub>3</sub>, and H<sub>2</sub>O. The water vapor can come from adsorbed water or from zeolite dehydroxylation or can be added as reactant to the solids. The exchange from In<sub>2</sub>O<sub>3</sub> is promoted by hydrogen, facilitating indium reduction and InOH formation. In high silica zeolites, such as mordenite, the indium is stabilized as an exchange cation; i.e., the In<sup>+</sup> is not reduced to In<sup>0</sup> by H<sub>2</sub> up to 973 K. However, the In<sup>+</sup> cations are readily oxidized by O<sub>2</sub> or H<sub>2</sub>O to In<sup>3+</sup> oxycations that can be reversibly reduced by H<sub>2</sub>. The In-zeolites are good oxygen carriers and promising redox catalysts.

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## References and Notes

- (1) Jacobs, P. A. *Carboniogenic Activity of Zeolites*; Elsevier: Amsterdam, Oxford, New York, 1977; p 7.
- (2) Romanowski, W.; Jablonski, J. M. In *Catalysis on Zeolites*; Kalló, D., Minachev, Kh. M., Eds.; Akadémiai Kiadó: Budapest, 1988; p 277.
- (3) Karge, H. G.; Beyer, H. K. *Stud. Surf. Sci. Catal.* **1991**, *69*, 43.
- (4) Kucherov, A. V.; Slinkin, A. A. *J. Mol. Catal.* **1994**, *90*, 323.
- (5) Karge, H. G. *Stud. Surf. Sci. Catal.* **1997**, *105*, 1901.
- (6) Seidel, A.; Bodenberger, B. *Chem. Phys. Lett.* **1996**, *249*, 117.
- (7) Onyestyák, Gy.; Lónyi, F.; Valyon, J. *J. Therm. Anal. Calorim.* **2005**, *79*, 561.
- (8) Ogura, M.; Ohsaki, T.; Kikuchi, E. *Microporous Mesoporous Mater.* **1998**, *21*, 533.
- (9) Ramallo-López, J. M.; Gutierrez, L. B.; Bibiloni, A. G.; Requejo, F. G.; Miró, E. E. *Catal. Lett.* **2002**, *82*, 131.
- (10) Maunula, T.; Ahola, J.; Hamada, H. *Appl. Catal. B: Environ.* **2006**, *64*, 13.
- (11) Anunziata, O. A.; Beltramone, A. R.; Ledo, E. J.; Requejo, F. G. *J. Mol. Catal. A: Chem.* **2007**, *267*, 272.
- (12) Price, G. L.; Kanazirev, V. *J. Catal.* **1990**, *126*, 267.
- (13) Halász, J.; Nyári, W.; Meretei, E.; Hannus, I.; Nagy, J. B.; Kiricsi, I. *J. Mol. Struct.* **2003**, *651–653*, 315.



- (14) Mavrodinova, V.; Popova, M.; Mihályi, M. R.; Pál-Borbély, G.; Minchev, Ch. *Appl. Catal. A: Gen.* **2004**, *262*, 75.
- (15) Srdanov, V. I.; Blake, N. P.; Markgraber, D.; Metiu, H.; Stucky, G. D. *Advanced Zeolite Science and Applications, Studies in Surface Science and Catalysis*; Jansen, J. C., Stocker, M., Karge, H. G., Weitkamp, J., Eds.; Elsevier Science: Amsterdam, 1994; Vol. 85, pp 115–144.
- (16) Kanazirev, V.; Neinska, Y.; Tsoncheva, T.; Kosova, L. *Proc. 9th Int. Zeolite Conf.*; von Ballmoos, R., Higgins, J. B., Treacy, M. M. J., Eds.; Montreal 1992, Butterworth-Heinemann: London, 1993; p 461.
- (17) Beyer, H. K.; Mihályi, R. M.; Minchev, Ch.; Neinska, Y.; Kanazirev, V. *Microporous Mater.* **1996**, *7*, 333.
- (18) Mihályi, R. M.; Beyer, H. K.; Mavrodinova, V.; Minchev, Ch.; Neinska, Y. *Microporous Mesoporous Mater.* **1998**, *24*, 143.
- (19) Zhou, X.; Xu, Z.; Zhang, T.; Lin, L. *J. Mol. Catal. A: Chem.* **1997**, *122*, 125.
- (20) Kikuchi, E.; Ogura, M.; Terasaki, I.; Goto, Y. *J. Catal.* **1996**, *161*, 465.
- (21) Kanazirev, V.; Price, G. L.; Dooley, K. M. *Stud. Surf. Sci. Catal.* **1991**, *69*, 277.
- (22) Kanazirev, V.; Price, G. L. *Stud. Surf. Sci. Catal.* **1994**, *84*, 1935.
- (23) Price, G. L.; Kanazirev, V.; Church, D. F. *J. Phys. Chem.* **1995**, *99*, 864.
- (24) Kanazirev, V.; Valtchev, V.; Tarassov, M. P. *J. Chem. Soc., Chem. Commun.* **1994**, 1043.
- (25) Zecchina, A.; Geobaldo, F.; Spoto, G.; Bordiga, S.; Ricchiardi, G.; Buzzoni, R.; Petrini, G. *J. Phys. Chem.* **1996**, *100*, 16584.
- (26) Mihályi, M. R.; Beyer, H. K. *Chem. Commun.* **2001**, 2242.
- (27) Grigorieva, T. F.; Barinova, A. P.; Lyakhov, N. Z. *J. Nanoparticle Res.* **2003**, *5*, 439.
- (28) *Gmelins Handbuch der Anorganischen Chemie*; Verlag Chemie, G.M.B.H.: Berlin, 1936; Vol. 37, pp 65.
- (29) Lakin, N. M.; Brown, J. M.; Beattie, I. A.; Jones, P. J. *J. Chem. Phys.* **1994**, *100*, 8546.
- (30) Yamada, M. *Chem. Phys. Lett.* **1997**, *280*, 535.
- (31) Neinska, Y.; Mavrodinova, V.; Minchev, Ch.; Mihályi, M. R. *Stud. Surf. Sci. Catal.* **1999**, *125*, 37.

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