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# Propane dehydrogenation over extra-framework In(I) in chabazite zeolites†

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Indium on silica, alumina and zeolite chabazite (CHA), with a range of In/Al ratios and Si/Al ratios, have been investigated to understand the effect of the support on indium speciation and its corresponding influence on propane dehydrogenation (PDH). It is found that  $\text{In}_2\text{O}_3$  is formed on the external surface of the zeolite crystal after the addition of  $\text{In}(\text{NO}_3)_3$  to H-CHA by incipient wetness impregnation and calcination. Upon reduction in  $\text{H}_2$  gas (550 °C), indium displaces the proton in Brønsted acid sites (BASs), forming extra-framework  $\text{In}^+$  species (In-CHA). A stoichiometric ratio of 1.5 of formed  $\text{H}_2\text{O}$  to consumed  $\text{H}_2$  during  $\text{H}_2$  pulsed reduction experiments confirms the indium oxidation state of +1. The reduced indium is different from the indium species observed on samples of  $10\text{In}/\text{SiO}_2$ ,  $10\text{In}/\text{Al}_2\text{O}_3$  (i.e., 10 wt% indium) and bulk  $\text{In}_2\text{O}_3$ , in which  $\text{In}_2\text{O}_3$  was reduced to  $\text{In}(0)$ , as determined from the X-ray diffraction patterns of the product,  $\text{H}_2$  temperature-programmed reduction ( $\text{H}_2$ -TPR) profiles, pulse reactor investigations and *in situ* transmission FTIR spectroscopy. The BASs in H-CHA facilitate the formation and stabilization of  $\text{In}^+$  cations in extra-framework positions, and prevent the deep reduction of  $\text{In}_2\text{O}_3$  to  $\text{In}(0)$ .  $\text{In}^+$  cations in the CHA zeolite can be oxidized with  $\text{O}_2$  to form indium oxide species and can be reduced again with  $\text{H}_2$  quantitatively. At comparable conversion, In-CHA shows better stability and  $\text{C}_3\text{H}_6$  selectivity (~85%) than  $\text{In}_2\text{O}_3$ ,  $10\text{In}/\text{SiO}_2$  and  $10\text{In}/\text{Al}_2\text{O}_3$ , consistent with a low  $\text{C}_3\text{H}_8$  dehydrogenation activation energy (94.3 kJ mol<sup>-1</sup>) and high  $\text{C}_3\text{H}_8$  cracking activation energy (206 kJ mol<sup>-1</sup>) in the In-CHA catalyst. A high Si/Al ratio in CHA seems beneficial for PDH by decreasing the fraction of CHA cages containing multiple  $\text{In}^+$  cations. Other small-pore zeolite-stabilized metal cation sites could form highly stable and selective catalysts for this and facilitate other alkane dehydrogenation reactions.

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## Introduction

The increasing world demand for propylene and the current low cost of propane derived from shale gas have renewed interest in the propane dehydrogenation reaction (PDH).<sup>1</sup> PDH technologies, i.e., the Catofin process using a  $\text{CrO}_x/\text{Al}_2\text{O}_3$  catalyst, and the Oleflex process using a supported Pt–Sn catalyst, have drawbacks, such as the high cost and rapid deactivation of Pt and the potential environmental impact caused by Cr. Many other catalysts for PDH have been investigated including Ga-,<sup>2–10</sup> Zn-,<sup>11,12</sup> Co-,<sup>13–15</sup> Fe-,<sup>16–18</sup> V-,<sup>19–22</sup> Zr-based materials,<sup>23–25</sup> and nanocarbon catalysts.<sup>26,27</sup> Metal cations ( $\text{Ga}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ , etc.) exchanged in zeolite H-ZSM-5<sup>28–32</sup> have shown promising alkane dehydrogenation properties as well: among them, Ga/H-ZSM-5 exhibits high stability and high propylene selectivity (~90%) for propane dehydrogenation.<sup>31,32</sup>

Shimizu and coworkers<sup>33,34</sup> recently reported that In-CHA is a stable and selective catalyst for ethane dehydrogenation. They

have also shown that the CHA zeolite is superior to other zeolite frameworks for this reaction (BEA, MFI, and MOR) and that an Al-rich In-CHA zeolite (Si/Al = 6.85) provided higher dehydrogenation rates. They showed that  $\text{In}_2\text{O}_3$ , initially present on the external surface of CHA, can be reduced and then reacts with the Brønsted acid sites (BASs) of the zeolite to form an indium-exchanged ( $\text{In}^+$ ) CHA catalyst through the so-called reductive solid-state-ion exchange (RSSIE) process. Isolated  $[\text{InH}_2]^+$  sites were put forward as the active center in these catalysts based on Fourier transform infrared (FTIR) spectroscopy and X-ray absorption fine structure (XAFS) measurements.

The identification of  $[\text{InH}_2]^+$  as the active site for ethane dehydrogenation was primarily based on *ex situ* FTIR spectroscopy and DFT calculations;<sup>33,34</sup> however, the spectra used in support of the presence of  $[\text{InH}_2]^+$  were collected at low temperature (below 153 K, after treating with  $\text{H}_2$  at 773 K), and therefore whether the indium hydride is stable at the reaction temperature (600 °C) remains to be determined. Furthermore, Andrews *et al.*<sup>35</sup> have found that indium hydride is unstable at temperatures above 200 K (indium hydride forms at 3.5 K but disappears above 200–210 K). It is thus uncertain whether  $[\text{InH}_2]^+$  is an intermediate at catalytic reaction temperatures. This point has also been debated in Ga/H-ZSM-5 catalysts with

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respect to propane dehydrogenation. Bell and coworkers<sup>32</sup> believe that single  $[\text{GaH}]^{2+}$  sites are the active species; however, Schreiber *et al.*<sup>31</sup> reported that  $\text{Ga}^+-\text{H}^+$  pair sites are the stable active sites, a model supported by results from our laboratory.<sup>36</sup> Phadke *et al.*<sup>32,37</sup> have pointed out that Ga-exchanged species associated with Al-pairs in Ga/H-MFI catalyze both propane and butane dehydrogenation while isolated Ga species did not. They found, however, that both Ga species exhibited similar properties for ethane dehydrogenation. It is thus possible that the reaction mechanism of propane dehydrogenation with the In-CHA catalyst is different from that of ethane dehydrogenation.

Hart *et al.*<sup>38</sup> reported that MFI-supported catalysts containing high indium loadings (In/Al ratio close to 1 to minimize the presence of BASs) selectively catalyze the propane dehydrogenation reaction, but the reduction of indium species to In(0) during the reaction resulted in catalyst deactivation. Jones and coworkers<sup>39,40</sup> investigated  $\text{In}_2\text{O}_3$ - $\text{Ga}_2\text{O}_3$  and ternary In-Ga-Al mixed oxides as catalysts for propane dehydrogenation and found that reducing  $\text{In}_2\text{O}_3$  domains to In(0) was detrimental to catalytic performance, and that once In(0) is formed from  $\text{In}_2\text{O}_3$ , it cannot be reactivated, indicating that In(0) was inactive for propane activation. These reports show that indium speciation at high temperature is highly dependent on the catalyst support: CHA-supported indium was stable for ethane dehydrogenation for 90 h time-on-stream (TOS), while the  $\text{Al}_2\text{O}_3$  supported indium catalyst deactivated with time on stream.<sup>33,39</sup> Understanding the support impact on indium speciation and the corresponding influence on catalytic performance is thus important to advance In-based catalyst understanding for alkane dehydrogenation reactions.

In this work, samples of indium on silica, on alumina and exchanged into CHA zeolites with varying In/Al ratios and Si/Al ratios have been used to investigate the effect of the support on the indium speciation and the corresponding impact on propane dehydrogenation rates. On In-CHA,  $\text{In}_2\text{O}_3$  initially located on the external surface of the H-CHA zeolite is reduced in the presence of dihydrogen displacing the protons of the BAS. Isolated  $\text{In}^+$  in the CHA zeolite was formed upon reduction. The reduced indium species were different on In/ $\text{SiO}_2$ , In/ $\text{Al}_2\text{O}_3$  and bulk  $\text{In}_2\text{O}_3$ , where a portion of  $\text{In}_2\text{O}_3$  was reduced to In(0) species. At comparable conversion, the propane dehydrogenation reaction over In-CHA shows better stability and  $\text{C}_3\text{H}_6$  selectivity ( $\sim 85\%$ ) than In/ $\text{SiO}_2$ , In/ $\text{Al}_2\text{O}_3$  and bulk  $\text{In}_2\text{O}_3$ . The examination of Si/Al ratios suggests that higher Si/Al ratios are beneficial to propane dehydrogenation. These results all point to the conclusion that the dehydrogenation properties of isolated  $\text{In}^+$  in CHA are superior to those of In(0) on other supports.

## Results and discussion

### Reduction of In-based catalysts

Indium supported on the CHA zeolite with varying In/Al ratios and Si/Al ratios,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$  are prepared as follows: H-CHA(11) samples were obtained *via* calcination of commercial  $\text{NH}_4\text{-CHA}$  (Si/Al = 11) samples obtained from ACS Material. H-CHA(*x*) (*x* = 5, 12 or 25, is the Si/Al ratio) were synthesized based on previous reports<sup>41,42</sup> (details are included in the ESI†). The

physical properties of H-CHA samples are summarized in Table S1.† The micropore volume of H-CHA samples is in the range of  $0.25\text{--}0.30\text{ cm}^3\text{ g}^{-1}$ , consistent with typical CHA zeolites' properties.<sup>43,44</sup> For the sample H-CHA(11), the  $^{27}\text{Al}$  solid-state nuclear magnetic resonance (SS-NMR) spectrum was dominated by a strong sharp signal at 54 ppm, which is assigned to tetrahedrally coordinated framework Al in the zeolite, and a weak feature at  $\sim 0$  ppm in the  $^{27}\text{Al}$  MAS NMR spectrum (Fig. S2†) is assigned to a small amount of extra-framework Al ( $\text{Al}_{\text{EF}}$ ), as octahedral aluminum (around 15%). Similarly, tetrahedrally coordinated Al is predominant in the spectra of the synthesized H-CHA with varying Si/Al ratios, and almost no  $\text{Al}_{\text{EF}}$  was observed at Si/Al ratios of 12 and 25.<sup>44</sup> The SEM images (Fig. S3†) of the CHA sample show approximately 300 nm, 300 nm, 1  $\mu\text{m}$ , and 1.5  $\mu\text{m}$  sized zeolite crystals for H-CHA(11), H-CHA(5), H-CHA(12), and H-CHA(25), respectively. The surface area of  $\text{SiO}_2$  and  $\gamma\text{-Al}_2\text{O}_3$  investigated was 285 and  $79\text{ m}^2\text{ g}^{-1}$  (Table S2†). The composition of In-based catalysts including In-CHA with varying In/Al and Si/Al ratios and 10In/ $\text{SiO}_2$  and 10In/ $\text{Al}_2\text{O}_3$  is summarized in Table S3.†

The XRD patterns of the In-based catalyst before and after reduction confirm that the indium phase formed after reduction is highly dependent on the support. The expected diffraction peaks of the CHA zeolite (Fig. 1 and S4†) are observed for all H-CHA samples investigated,<sup>43</sup> verifying that all zeolite samples are pure in phase and highly crystalline. The peaks of the  $\text{In}_2\text{O}_3$  phase (JCPDS 06-0416) are clearly observed on the In-CHA(11, 1.0), 10In/ $\text{Al}_2\text{O}_3$  and 10In/ $\text{SiO}_2$  samples, prepared *via* the incipient wetness impregnation method, followed by calcination at 600  $^\circ\text{C}$  (the *x* and *y* in In-CHA(*x*, *y*) represent the Si/Al ratio and In/Al ratio, respectively). Upon reduction at 600  $^\circ\text{C}$ , the  $\text{In}_2\text{O}_3$  peaks on the impregnated + calcined H-CHA sample disappear (Fig. 1) without another indium-related phase detected by XRD. This shows that  $\text{In}_2\text{O}_3$  supported on the CHA zeolite is reduced to form highly dispersed species. The decrease in the relative intensity between the diffraction peaks at  $\sim 9^\circ$  and  $\sim 21^\circ$  on reduced In-CHA(11, 1.0) was interpreted as the introduction of extra-framework indium cations when exchanged with BASs (results below support the formation of

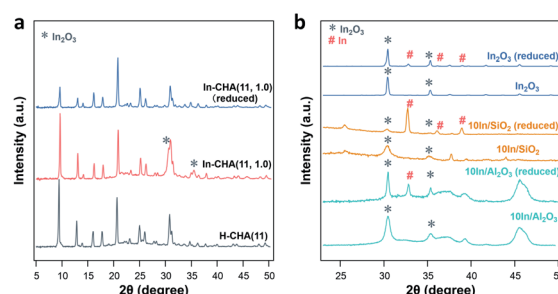


Fig. 1 XRD patterns of samples investigated after calcination and reduction: (a) H-CHA(11) and In-CHA(11, 1.0); (b) indium on silica and alumina and bulk  $\text{In}_2\text{O}_3$ . The diffraction peaks at  $2\theta$  values of  $30.6^\circ$  and  $35.5^\circ$  (marked with asterisks) are assigned to  $\text{In}_2\text{O}_3$  (JCPDS 060416), and diffraction peaks at  $2\theta$  values of  $33.0^\circ$ ,  $36.3^\circ$  and  $39.2^\circ$  (marked with #) are associated with In(0) (JCPDS 05-0642).



$\text{In}^+$ ). Similar observations were made on  $\text{In-CHA}(x, 1.0)$  ( $x = 5, 12$  and  $25$ , as shown in Fig. S4†). The micropore volumes of  $\text{In-CHA}(11, 1.0)$ , calcined and reduced, are  $0.21$  and  $0.20 \text{ cm}^3 \text{ g}^{-1}$ , respectively (Table S1†). Considering the presence of indium species inside the micropores when calculating the micropore volume, by subtracting the mass of indium in  $\text{In-CHA}(11, 1.0)$  and assuming that  $\text{In}_2\text{O}_3$  and  $\text{In}^+$  sites were formed in the calcined and reduced samples, the micropore volumes (without the In mass in them) were recalculated to be  $0.26$  and  $0.23 \text{ cm}^3 \text{ g}^{-1}$ , respectively. The similar micropore volume of  $\text{In-CHA}(11, 1.0)$  and  $\text{H-CHA}(11)$  suggests that  $\text{In}_2\text{O}_3$  is largely located on the external surface of the  $\text{H-CHA}(11)$  zeolite particles, rather than inside the micropores, before reduction. The lower micropore volume of reduced  $\text{In-CHA}(11, 1.0)$  compared to  $\text{H-CHA}(11)$  suggests that indium species moved into the micropores of the zeolite upon reduction. A significant fraction of micropores were occupied by indium species on reduced  $\text{In-CHA}(5, 1.0)$  compared with  $\text{H-CHA}(5)$  ( $0.27$  versus  $0.16 \text{ cm}^3 \text{ g}^{-1}$ , shown in Table S1†), which is due to a large amount of  $\text{In}_2\text{O}_3$  that diffused into the micropores of the zeolite, while the void fraction occupation of micropores was low on reduced  $\text{In-CHA}(25, 1.0)$  samples. The diffusion of  $\text{In}_2\text{O}_3$  into the zeolite micropores is also supported by the SEM and TEM images of calcined and reduced  $\text{In-CHA}$  (see Fig. S3 and S5†). The  $\text{In}_2\text{O}_3$  particles observed on the external surface of the  $\text{CHA}$  particles (bright spots in SEM images and dark spots in TEM images) nearly disappear after reduction (Fig. S3 and S5†). Note that  $\text{In}_2\text{O}_3$  particles are larger than  $2 \text{ nm}$  and thus cannot enter the small micropores of  $\text{CHA}$ . The exchange process was assisted by  $\text{H}_2$  reduction, usually referred to as the RSSIE process.<sup>33,34</sup> The  $\text{In}_2\text{O}_3$  phase could have been reduced to  $\text{In}_2\text{O}$ , which is volatile and can diffuse into the micropores of  $\text{CHA}$  where it reacts with BASs forming  $\text{In}^+$  sites. A similar process was also reported by Ga oxide in Ga/H-ZSM-5 systems.<sup>45,46</sup> The  $^{27}\text{Al}$  NMR spectrum of reduced  $\text{In-CHA}$  with different Si/Al ratios showed a broadened peak at  $54 \text{ ppm}$  (tetrahedrally coordinated Al), assigned to a distorted tetrahedral aluminum environment.<sup>47,48</sup>

It follows that upon reduction of  $\text{In-CHA}$ , the indium species enter the pores of the zeolite and interact with tetrahedrally coordinated Al. When indium is impregnated on  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  supports,  $\text{In}(0)$  was formed upon reduction (Fig. 1). But note that not all  $\text{In}_2\text{O}_3$  is reduced since both  $\text{In}_2\text{O}_3$  and  $\text{In}(0)$  are detected (Fig. 1). The pristine  $\text{In}_2\text{O}_3$  sample initially displays only the  $\text{In}_2\text{O}_3$  phase, and upon reduction  $\text{In}(0)$  is formed despite the remaining presence of a large amount of  $\text{In}_2\text{O}_3$ .  $\text{In}(0)$  is the species observed on bulk  $\text{In}_2\text{O}_3$  and indium supported on silica and alumina although not all  $\text{In}_2\text{O}_3$  could be reduced under the conditions investigated ( $10 \text{ vol}\% \text{ H}_2/\text{N}_2$  at  $600^\circ\text{C}$  for  $30 \text{ min}$ ), which is very different from the case of  $\text{CHA}$ . As the In/Al ratio of  $\text{In-CHA}$  (Si/Al =  $12$ ) rises from  $0.3$  to  $1.7$ , the  $\text{In}_2\text{O}_3$  diffraction peaks on calcined samples become gradually more clear (Fig. S6†). Upon reduction,  $\text{In}_2\text{O}_3$  diffraction peaks disappear when the In/Al ratio is at or below  $1.0$ . Both  $\text{In}_2\text{O}_3$  and  $\text{In}(0)$  diffraction peaks, however, are detected upon reducing  $\text{In-CHA}(12, 1.7)$ ; that is,  $\text{In}_2\text{O}_3$  is partially reduced to form  $\text{In}(0)$  when the BASs become scarce, as observed in bulk  $\text{In}_2\text{O}_3$  and indium loaded on  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ .

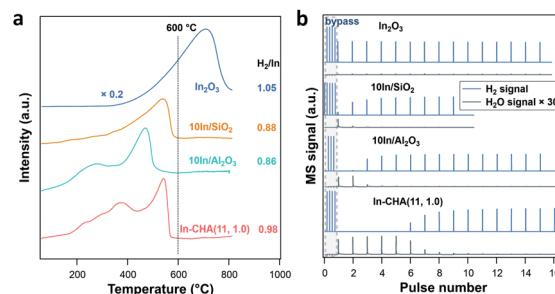


Fig. 2 (a)  $\text{H}_2$ -TPR profiles and (b) results of  $\text{H}_2$  pulse experiments on In-based catalyst at  $600^\circ\text{C}$ .

Table 1 Quantification of  $\text{H}_2$  consumption from  $\text{H}_2$ -TPR profiles and  $\text{H}_2$  pulses and corresponding  $\text{O}_2$  consumption from  $\text{O}_2$  pulses

Sample	$\text{H}_2/\text{In}$ ( $\text{H}_2$ -TPR)	$\text{H}_2/\text{In}$ ( $\text{H}_2$ -pulse)	$\text{O}/\text{In}$ ( $\text{O}_2$ pulse)
$\text{In}_2\text{O}_3$	1.05	—	—
$10\text{In}/\text{SiO}_2$	0.88	$0.25 \pm 0.02$	$0.12 \pm 0.01$
$10\text{In}/\text{Al}_2\text{O}_3$	0.86	$0.46 \pm 0.01$	$0.44 \pm 0.02$
$\text{In-CHA}(11, 1.0)$	0.98	$0.86 \pm 0.02$	$0.86 \pm 0.02$
$\text{In-CHA}(11, 1.0)$ , ( $\text{H}_2$ - $\text{O}_2$ treated)	—	$0.92 \pm 0.02$	$0.92 \pm 0.02$

$\text{H}_2$ -TPR measurements were conducted to monitor the reduction process of the In-based catalyst (Fig. 2a). For  $\text{In-CHA}(11, 1.0)$ , the resulting profile shows several peaks with increasing temperature from  $200^\circ\text{C}$  to  $600^\circ\text{C}$ . This complex signal may result from two factors: (1) the distribution of  $\text{In}_2\text{O}_3$  particle sizes at a high In loading ( $\sim 14\%$ ) had a variety of reduction temperatures;<sup>40</sup> (2) an elevated temperature was needed to drive the reaction of  $\text{In}_2\text{O}_3$  with BASs when the sites had been consumed mainly at lower temperatures. On  $10\text{In}/\text{SiO}_2$  and  $10\text{In}/\text{Al}_2\text{O}_3$  catalysts, the reduction profile shows complete reduction below  $600^\circ\text{C}$ . Bulk  $\text{In}_2\text{O}_3$ , however, shows a much higher reduction temperature with the reduction peak centered at around  $700^\circ\text{C}$ ; that is, bulk  $\text{In}_2\text{O}_3$  is harder to reduce (consistent with the observation of Jones and coworkers).<sup>39</sup> The higher reduction temperature explains the large amount of  $\text{In}_2\text{O}_3$  observed by XRD after reducing the  $\text{In}_2\text{O}_3$  catalyst (Fig. 1).

The quantification of the  $\text{H}_2/\text{In}$  ratio during the  $\text{H}_2$ -TPR experiments provides information about the reaction stoichiometry and composition of the reduced indium species (Table 1). The consumed  $\text{H}_2/\text{In}$  ratio on the  $\text{In-CHA}(11, 1.0)$  catalyst was  $0.98$ ; almost all  $\text{In}_2\text{O}_3$  species were reduced to  $\text{In}^+$ . However, the  $\text{H}_2/\text{In}$  ratio on  $10\text{In}/\text{SiO}_2$  and  $10\text{In}/\text{Al}_2\text{O}_3$  was  $0.88$  and  $0.86$ , respectively. The fact that the  $\text{H}_2/\text{In}$  ratio is less than unity shows that not all  $\text{In}_2\text{O}_3$  was reduced. Combined with the XRD measurements, it is concluded that only a fraction of  $\text{In}_2\text{O}_3$  on  $10\text{In}/\text{SiO}_2$  and  $10\text{In}/\text{Al}_2\text{O}_3$  was reduced to form  $\text{In}(0)$ , which appears to hinder the further reduction of the remaining  $\text{In}_2\text{O}_3$  and results in the low  $\text{H}_2/\text{In}$  ratios observed. A higher  $\text{H}_2/\text{In}$  ratio is observed on  $\text{In}_2\text{O}_3$  than on  $10\text{In}/\text{SiO}_2$  and  $10\text{In}/\text{Al}_2\text{O}_3$  although



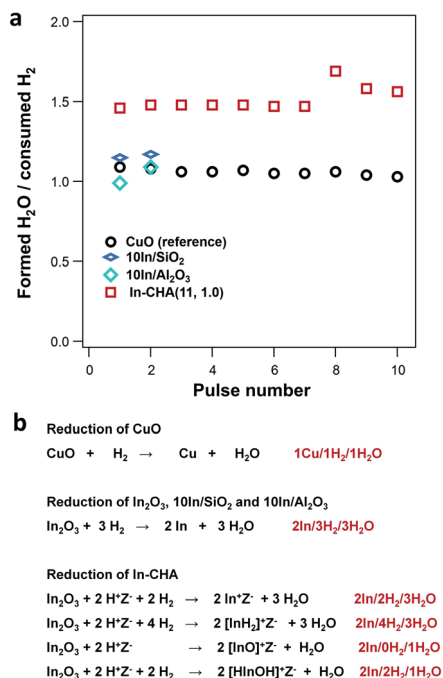


Fig. 3 (a) Determination of the formed H<sub>2</sub>O/consumed H<sub>2</sub> ratio from H<sub>2</sub> pulses as a function of pulse number on several catalysts. (b) Stoichiometric analysis during reduction on CuO, In<sub>2</sub>O<sub>3</sub>, 10In/SiO<sub>2</sub>, and 10In/Al<sub>2</sub>O<sub>3</sub>, and potential reactions on In-CHA catalysts.

the major consumption of H<sub>2</sub> occurs at elevated temperature (>600 °C).

H<sub>2</sub> pulse experiments provide additional details about the reduction process. As shown in Fig. 2b, the initial 5 H<sub>2</sub> pulses were completely consumed on In-CHA(11, 1.0), and occurred in parallel with the formation of H<sub>2</sub>O, confirming that the reduction process consumes H<sub>2</sub> and forms H<sub>2</sub>O. The quantified H<sub>2</sub> to In content ratio was 0.86, slightly lower than 1. The slightly smaller H<sub>2</sub>/In ratio in the H<sub>2</sub>-pulse experiments *versus* the H<sub>2</sub> consumed in the H<sub>2</sub>-TPR profiles is probably due to a small fraction of In<sub>2</sub>O<sub>3</sub> that was not reduced *via* H<sub>2</sub> pulses. To test this hypothesis, we reduced In-CHA(11, 1.0) using a 10 vol% H<sub>2</sub> flow for 30 min, followed by O<sub>2</sub> pulses (Fig. S7†) and found that the O/In ratio was 1.01, consistent with the analysis of the H<sub>2</sub>-TPR profiles. On the 10In/Al<sub>2</sub>O<sub>3</sub>, 10In/SiO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> samples, the H<sub>2</sub> consumption in the H<sub>2</sub> pulses decreases gradually with the pulse number (Fig. 2b and Table 1). The H<sub>2</sub>/In ratios are lower than the values obtained from H<sub>2</sub>-TPR, suggesting that H<sub>2</sub> pulses cannot completely reduce the sample (possibly due to the dilution by the carrier gas) compared with experiments under a constant H<sub>2</sub> flow. The O/In ratio of In-CHA(11, 1.0) was consistent with H<sub>2</sub>/In ratios (Table 1), demonstrating the quantitative reduction/oxidation of the In<sup>+3</sup>/In<sup>+</sup> cations in the In-CHA samples.

On 10In/SiO<sub>2</sub> and 10In/Al<sub>2</sub>O<sub>3</sub> catalysts, the lower O/In ratio *versus* the H<sub>2</sub>/In ratio may result from the slow oxidation kinetics during O<sub>2</sub> pulses (Table 1 and Fig. S8†). These experiments demonstrate that over CHA zeolites, the reduction of In<sub>2</sub>O<sub>3</sub> to In<sup>+</sup> prevents the deep reduction of In<sub>2</sub>O<sub>3</sub> to In(0). Once

In<sup>+</sup> is formed in the extra-framework positions of the CHA zeolite, it can be oxidized quantitatively to In<sup>3+</sup> through oxygen pulses consuming 1 oxygen atom per In cation (denoted as H<sub>2</sub>-O<sub>2</sub> treated, shown in Table 1 and Fig. S7†), and then reduced quantitatively, consuming one dihydrogen molecule per In cation.

### Identification of isolated In<sup>+</sup> sites

We have employed a pulse-reactor and *in situ* FTIR spectroscopy to determine that isolated In<sup>+</sup> sites are the stable species formed upon reduction of the In-CHA catalyst with H<sub>2</sub>. In fact, the ratio between the formed H<sub>2</sub>O and consumed H<sub>2</sub> at the reaction temperature is consistent with isolated In<sup>+</sup> sites as the stable indium species: as shown in Fig. 3a, the ratio of formed H<sub>2</sub>O/consumed H<sub>2</sub> was 1.5 for the impregnated/calcined In<sub>2</sub>O<sub>3</sub>/CHA. As a control experiment, the formed H<sub>2</sub>O/consumed H<sub>2</sub> ratio on CuO was determined to be ~1.0, which is consistent with the stoichiometry during reduction (Fig. 3b and S9†). The higher ratio of formed H<sub>2</sub>O/consumed H<sub>2</sub> means that another H source contributes to the H<sub>2</sub>O formation during the reduction process on In-CHA. It follows that In<sub>2</sub>O<sub>3</sub> is reduced to In(i) and then exchanged for protons in CHA. Based on the list of possible reactions (Fig. 3b), it is concluded that In<sup>+</sup> sites were the product of In<sub>2</sub>O<sub>3</sub> reduction, rather than [InH<sub>2</sub>]<sup>+</sup>, [InO]<sup>+</sup> or [HinOH]<sup>+</sup> (Fig. 3b).

On 10In/SiO<sub>2</sub> and 10In/Al<sub>2</sub>O<sub>3</sub>, the formed H<sub>2</sub>O/consumed H<sub>2</sub> ratio in the initial H<sub>2</sub> pulse experiment was 1.0, which means that In<sub>2</sub>O<sub>3</sub> reacted with H<sub>2</sub> to form In(0) and H<sub>2</sub>O (Fig. 3b). These results are consistent with the identification of In(0) crystals in the XRD patterns of the reduced samples. Schreiber *et al.*<sup>31</sup> applied the same technique to determine that Ga<sup>+</sup> is the dominant species formed after reducing Ga/ZSM-5. Our results provide another example of the application of a pulse reactor to identify the structure and oxidation state of the metal-exchanged zeolite.

The determination of consumed H<sub>2</sub> on In-CHA with varying Si/Al ratios and In/Al ratios demonstrates that In<sub>2</sub>O<sub>3</sub> could be completely reduced to In<sup>+</sup> species when the In/Al ratios ≤ 1.0,

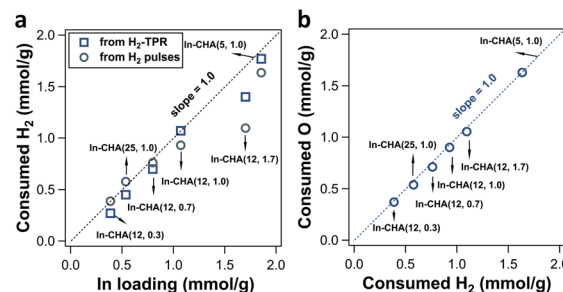


Fig. 4 (a) Quantification of consumed H<sub>2</sub> from H<sub>2</sub> pulses (black circle point) and H<sub>2</sub>-TPR (blue square point) over In-CHA(x, y) (as indicated in the figure). The black dotted line represents the ratio of consumed H<sub>2</sub> to In loading of 1. (b) Quantification of consumed O atoms from O<sub>2</sub> pulses as a function of consumed H<sub>2</sub> from H<sub>2</sub> pulses over In-CHA(x, y) (as indicated in the figure). The blue dotted line represents a ratio of consumed O to consumed H<sub>2</sub> of 1. The corresponding H<sub>2</sub>-TPR profiles and H<sub>2</sub> pulse and O<sub>2</sub> pulse curves are shown in Fig. S10 and S11.†



independent of Si/Al ratios. For In-CHA (Si/Al = 12) with varying In/Al ratios (Fig. 4a and S10†), the H<sub>2</sub> consumption determined from H<sub>2</sub> pulses and H<sub>2</sub>-TPR profiles *versus* In loading falls on a straight line with a slope of 1.0 when the In/Al ratio is at or below 0.7. This slope suggests that In<sub>2</sub>O<sub>3</sub> was chiefly reduced to In<sup>+</sup>.

As the In/Al ratio rises to 1.0, the H<sub>2</sub>/In ratio determined from H<sub>2</sub>-TPR profiles reached 1.0, consistent with the result of the In-CHA(11, 1.0) catalyst. A H<sub>2</sub>/In ratio slightly lower than 1.0 from the H<sub>2</sub> pulses is due to the dilution by the carrier gas when using H<sub>2</sub> pulses as the reducing agent. Further increase of the In/Al ratio to 1.7 results in a lower H<sub>2</sub>/In ratio as determined from both H<sub>2</sub>-TPR profiles and H<sub>2</sub> pulses; that is, the excess of In<sub>2</sub>O<sub>3</sub> cannot be reduced completely, a result that is consistent with the detection of In(0) and In<sub>2</sub>O<sub>3</sub> on the reduced In-CHA(12, 1.7) in XRD patterns (Fig. S6†). On In-CHA with different Si/Al ratios (Fig. 4a and S11†), the H<sub>2</sub>/In ratios are close to 1.0, confirming that In<sub>2</sub>O<sub>3</sub> in the CHA zeolite can be reduced to replace BASs and form isolated In<sup>+</sup> when In/Al ratios ≤ 1.0 (independently of the Si/Al ratio). A ratio between the formed H<sub>2</sub>O and consumed H<sub>2</sub> close to 1.5 for these In-CHA samples evidences the stoichiometry of the reaction during reduction (Fig. S12†).

Note that the small increase in the ratio of the formed H<sub>2</sub>O to consumed H<sub>2</sub> on In-CHA(12, 1.0) and In-CHA(12, 1.7) may result from the exchange of In<sub>2</sub>O<sub>3</sub> with BASs in the presence of H<sub>2</sub>, forming [InO]<sup>+</sup> and H<sub>2</sub>O. This process does not consume H<sub>2</sub>, but forms H<sub>2</sub>O. The exchange of In<sub>2</sub>O<sub>3</sub> with BASs is minor at high temperature (600 °C) since the formed [InO]<sup>+</sup> can be easily reduced to In<sup>+</sup>. Control experiments were conducted introducing H<sub>2</sub> pulses at different temperatures (200 °C to 600 °C, in Fig. S13†). No significant H<sub>2</sub> was consumed at or below 300 °C, but when the temperature was increased to 400 °C, the ratio of formed H<sub>2</sub>O to consumed H<sub>2</sub> reached 5.9, much higher than 1.5. This suggests that a significant fraction of In<sub>2</sub>O<sub>3</sub> was ion-exchanged with BASs to form [InO]<sup>+</sup>, accompanied by the formation of H<sub>2</sub>O without consuming H<sub>2</sub> (third possible reaction of the reduction of In-CHA in Fig. 3b). As the temperature rises to 500 °C, the ratio decreased to 1.39 in the initial H<sub>2</sub>

pulses; this is an effect due to two reactions: In<sub>2</sub>O<sub>3</sub> + 2H<sup>+</sup> + 2H<sub>2</sub> → 2In<sup>+</sup> + 3H<sub>2</sub>O and [InO]<sup>+</sup> + H<sub>2</sub> → In<sup>+</sup> + H<sub>2</sub>O. Further increase in temperature leads to a ratio between 1.0 and 1.5. It is concluded that different indium species were formed at different reduction temperatures. At 600 °C, In<sup>+</sup> is the stable species upon reduction of the In-CHA catalysts. The subsequent O<sub>2</sub> pulses on reduced In-CHA(x, y) also confirmed that In<sup>+</sup> is easy to oxidize (Fig. S10 and S11†). The ratio of O/H<sub>2</sub> was 1.0, showing that In<sup>3+</sup> was reduced to In<sup>+</sup> and then oxidized to In<sup>3+</sup> (Fig. 4b).

*In situ* FTIR spectroscopy reveals the consumption of BASs upon reduction of the In-CHA sample and clarifies the redox cycle of In-CHA catalysts in the presence of H<sub>2</sub> or O<sub>2</sub>. For the H-CHA sample (without indium, Fig. 5a(i)), two peaks at 3728 cm<sup>-1</sup> and 3575 cm<sup>-1</sup> are assigned to the external silanol group (Si-OH) and bridge-OH groups (BAS), respectively. As expected, there is no significant change before and after H<sub>2</sub> treatment (Fig. 5a(i) red and black traces). For In-CHA(11, 1.0), the spectrum of the dehydrated sample shows the same two peaks at 3728 cm<sup>-1</sup> and 3575 cm<sup>-1</sup>, but upon reduction at 550 °C, there is a clear reduction of the intensity of the peak at 3575 cm<sup>-1</sup>, evidence of the consumption of BASs after reducing In-CHA(11, 1.0). Additionally, there is a significant increase in the intensity of the zeolite structure Si-O-Si band at 1900–2100 cm<sup>-1</sup> (Fig. S14†), which might be due to the diffusion of a large amount of In<sub>2</sub>O<sub>3</sub> located initially on the outer surface into the micropores and strong bonding of In(i) to the zeolite oxygen atoms.

Interestingly, the peak at 3575 cm<sup>-1</sup> of the In-CHA(11, 1.0) catalyst did not disappear after reduction, and D<sub>2</sub> was used to determine if this peak is associated with OH groups. We found that the silanol group and the extra-framework Al-OH groups were converted to the corresponding -OD groups after coming into contact with D<sub>2</sub>; however, the peak at 3575 cm<sup>-1</sup> remains unmodified after D<sub>2</sub> treatment at 550 °C (Fig. S15†); that is, this

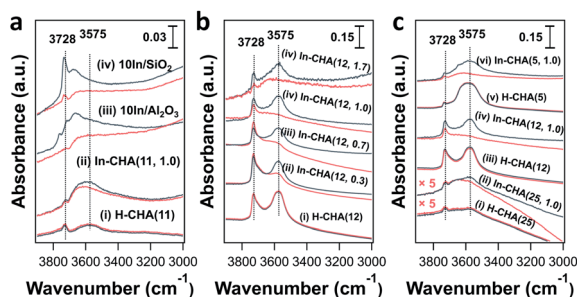


Fig. 5 FTIR spectra of In-containing catalysts and H-CHA collected during the H<sub>2</sub> reduction process at 550 °C: (a) indium on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, H-CHA(11) and In-CHA(11, 1.0), (b) In-CHA(12, y) with varying In/Al ratios ranging from 0 to 1.7, and (c) H-CHA(x) and In-CHA(x, 1.0) with varying Si/Al ratios ranging from 5 to 25 (see figure legends). Black and red traces represent spectra before and after reduction with H<sub>2</sub> (1 atm) at 550 °C, respectively. The background spectrum was collected in the IR cell, without a sample pellet, at room temperature under vacuum.

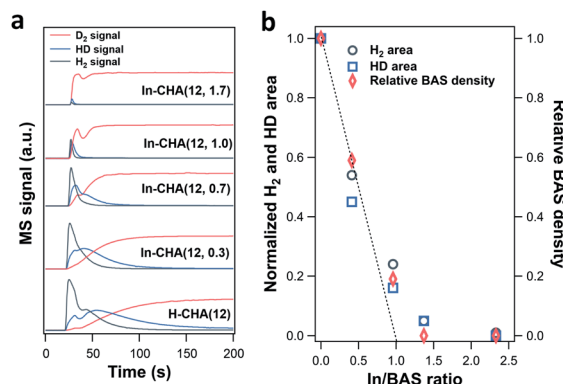


Fig. 6 (a) H<sub>2</sub> (2 amu), HD (3 amu), and D<sub>2</sub> (4 amu) signals as a function of time when switching the N<sub>2</sub> flow to a 10 vol% D<sub>2</sub> flow on In-CHA(12, y) with In/Al ratios ranging from 0 to 1.7 (see figure legends). The samples were reduced using a 10 vol% H<sub>2</sub>/N<sub>2</sub> flow for 30 min and purged with a N<sub>2</sub> flow for another 30 min before switching to a 10 vol% D<sub>2</sub> flow. (b) Integrated H<sub>2</sub> and HD peak area in (a) and relative BAS densities as a function of In/BAS ratios (normalized to the H<sub>2</sub> and HD peak area or BAS density of H-CHA(12)).



peak after reducing In-CHA(11, 1.0) is not from bridged-OH groups (*i.e.*, BAS). Even for H-CHA(11), the peak at  $3575\text{ cm}^{-1}$  still exists upon  $\text{D}_2$  treatment (Fig. S16<sup>†</sup>), suggesting that the observed peak may be unrelated to -OH groups. In the -OD region, there is no effect of  $\text{D}_2$  versus  $\text{H}_2$  treatment between  $1600\text{ cm}^{-1}$  and  $2000\text{ cm}^{-1}$  (Fig. S15c<sup>†</sup>). The lack of indium hydride vibrations also suggests that the isolated  $\text{In}^+$  site—rather than  $[\text{InH}_2]^+$ —was the dominant species formed upon reducing In-CHA at  $550^\circ\text{C}$  (Fig. S15c<sup>†</sup>). This is different from Ga/H-ZSM-5, where a significant  $\text{GaH}_x$  band is formed upon reduction at  $550^\circ\text{C}$ .<sup>45</sup>

In the samples of  $10\text{In}/\text{SiO}_2$  and  $10\text{In}/\text{Al}_2\text{O}_3$ , the hydroxyl group observed before reduction is largely consumed after reduction at  $550^\circ\text{C}$ , a consequence of the replacement of the proton in these sites by In species. The examination of reduced In-CHA with varying In/Al ratios and Si/Al ratios by FTIR spectroscopy also supported the consumption of BASs by the indium species (Fig. 5b, c and S17<sup>†</sup>). Meanwhile, no  $\text{InH}_x$  bands were observed on In-CHA( $x$ ,  $y$ ) with varying Si/Al and In/Al ratios ( $x = 5, 12$ , and  $25$  and  $y = 0.3, 0.7$  and  $1.0$ ), shown in Fig. S18–S22<sup>†</sup>, confirming that the only isolated  $\text{In}^+$  species were the stable In species in all In-CHA samples investigated.

The lower  $\text{H}^+$  concentration in reduced In-CHA samples compared with H-CHA is additional evidence showing that  $\text{In}^+$  species rather than  $\text{InH}_x$  were formed at  $550^\circ\text{C}$ . Note that the sample was first reduced in a 10 vol%  $\text{H}_2/\text{N}_2$  flow, followed by the purge of a pure  $\text{N}_2$  flow. Afterward, a 10 vol%  $\text{D}_2/\text{N}_2$  flow was introduced to measure the H concentration of the sample (including  $\text{H}_2$  and HD, 2 amu and 3 amu, respectively). For H-CHA(12) (Fig. 6a), significant  $\text{H}_2$  (2 amu) and HD (3 amu) MS signals were observed upon switching to 10 vol%  $\text{D}_2/\text{N}_2$ , due to the H–D exchange of the surface H species when introducing  $\text{D}_2$  into  $\text{H}_2$ -reduced H-CHA (see FTIR spectra in Fig. S15–S22<sup>†</sup>). Thus, the peak area of  $\text{H}_2$  (2 amu) and HD (3 amu) could be regarded as an indicator of the total H species on the samples.

The magnitude of the  $\text{H}_2$  and HD MS signals decreases gradually as the In/BAS ratio increases and almost disappears when the In/BAS ratio is 2.3 (corresponding to an In/Al ratio of 1.7, in Fig. S23<sup>†</sup>); that is, the addition of In to the CHA zeolite replaces the -OH group associated with BASs without forming indium hydrides (such as  $[\text{InH}_2]^+$ ) since more H species should be observed if one mol BAS was converted to one mol  $[\text{InH}_2]^+$ . The subsequent switching from 10 vol%  $\text{D}_2/\text{N}_2$  to 10 vol%  $\text{H}_2/\text{N}_2$  shows consistent results: the D concentration decreases as the In/Al ratio rises (Fig. S23<sup>†</sup>). We measured the BAS density *via* ethylamine-TPD of In-CHA(12,  $y$ ) (details are included in the ESI<sup>†</sup>). The relative BAS density *vs.* In/BAS ratio shows that one indium atom replaces one BAS, as concluded in the above discussions. The decreased  $\text{H}_2$ /HD concentration is similar to the relative BAS concentration with the increase of the In/BAS ratio, suggesting that the former may be used as an estimate for the relative BAS concentration on the In-CHA system.

FTIR spectroscopy of  $\text{d}_3$ -acetonitrile ( $\text{CD}_3\text{CN}$ ) adsorption provides information about the indium speciation of the reduced samples. In these experiments, the catalyst was reduced at  $550^\circ\text{C}$  for 30 min in pure  $\text{H}_2$  and cooled down to  $50^\circ\text{C}$  under vacuum, followed by the dosing of  $\text{CD}_3\text{CN}$ . As shown

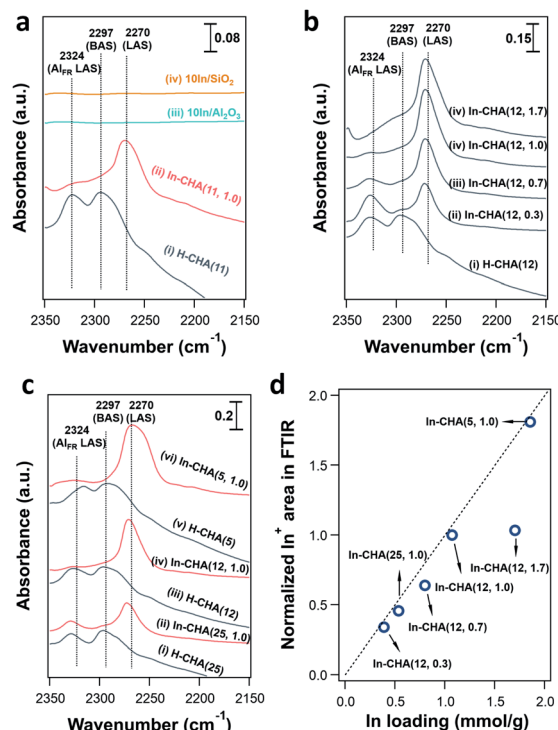


Fig. 7 FTIR spectra of the reduced In-based catalyst and H-CHA catalyst collected upon  $\text{CD}_3\text{CN}$  adsorption at  $50^\circ\text{C}$ : (a) In on  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , H-CHA(11) and In-CHA(11, 1.0), (b) In-CHA(12,  $y$ ) with In/Al ratios ranging from 0 to 1.7, and (c) H-CHA( $x$ ) and In-CHA( $x$ , 1.0) with Si/Al ratios ranging from 5 to 25 (see figure legends). The background spectrum was collected in the IR cell without a sample pellet at room temperature under vacuum. (d) Integrated  $\text{In}^+$  peak area of In-CHA( $x$ ,  $y$ ) catalysts with varying Si/Al ratios and In/Al ratios determined from infrared spectra (normalized to the  $\text{In}^+$  peak area of In-CHA(12, 1.0)) as a function of In loading.

in Fig. 7a, two peaks, at  $2324$  and  $2297\text{ cm}^{-1}$ , were observed on H-CHA(11), which were assigned to  $\text{CD}_3\text{CN}$  adsorbed on extra-framework Al and BASs, respectively.<sup>49</sup> This is consistent with the aluminum speciation determined from the  $^{27}\text{Al}$  MAS NMR spectra of the samples (Fig. S2<sup>†</sup>). Upon the introduction of  $\text{H}_2$  into In-CHA(11, 1.0), the peaks at  $2324$  and  $2297\text{ cm}^{-1}$  almost disappeared, confirming the consumption of BASs after reduction. Instead, a peak at  $2270\text{ cm}^{-1}$  appears, a signal attributed to the interactions of the nitrile group with Lewis acid sites (LASs). In the case of reduced In-CHA(11, 1.0), the LAS should be isolated  $\text{In}^+$  sites. For  $10\text{In}/\text{SiO}_2$  and  $10\text{In}/\text{Al}_2\text{O}_3$ , no well-defined peaks were observed upon  $\text{CD}_3\text{CN}$  adsorption on the reduced sample. This is attributed to the formation of  $\text{In}(0)$ , as observed in the corresponding XRD patterns and the pulse reactor experiments. For In-CHA (Si/Al = 12) with varying In/Al ratios, the peak intensity of isolated  $\text{In}^+$  species increases linearly as the In/Al ratio rises from 0.3 to 1.0 and stays constant with a further increase of the In/Al ratio to 1.7 (Fig. 7d); that is, the  $\text{In}^+$  density is related to the In loading and no more  $\text{In}^+$  species are formed when the BASs were replaced completely. A higher  $\text{In}^+$  species concentration is also observed on In-CHA(5, 1.0) (Fig. 7c and d) due to the higher In loadings.

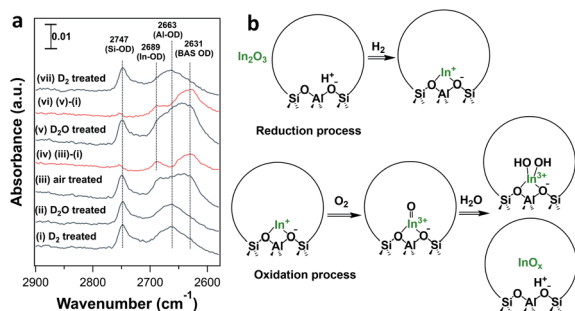


Fig. 8 (a) FTIR spectra of reduced In-CHA(11, 1.0) treated under different conditions at 550 °C: (i) D<sub>2</sub>; (ii) D<sub>2</sub>O; (iii) air; (iv) (i) subtracted from the spectrum (iii); (v) D<sub>2</sub>O; (vi) (i) subtracted from the spectrum (v); (vii) D<sub>2</sub>O. Background spectrum was collected in the spectral cell with the H<sub>2</sub> reduced sample pellet at 550 °C. (b) Proposed structures of exchanged In species in In-CHA upon reduction and subsequent oxidation.

*In situ* FTIR spectroscopy of the reduced and oxidized samples shows quantitative and reproducible oxidation/reduction of the In cation in In-CHA(11, 1.0). We introduced D<sub>2</sub> and D<sub>2</sub>O to facilitate the investigation of the reduction and oxidation of the sample. As shown in Fig. 8, two peaks at 2747 and 2643 cm<sup>-1</sup> were observed upon D<sub>2</sub> introduction (see Fig. S15†). When introducing D<sub>2</sub>O, there are no significant changes on the spectrum; that is, reduced In<sup>+</sup> sites do not react with D<sub>2</sub>O to form In-OD, clearly different from Ga/H-ZSM-5 where reduced Ga<sup>+</sup> was easy to oxidize to form Ga-OH at 550 °C with H<sub>2</sub>O.<sup>45</sup> Upon coming into contact with dry air, the BAS OD group (2631 cm<sup>-1</sup>) re-appears, a result of the regeneration of BASs when isolated In<sup>+</sup> was oxidized by air. From the difference spectrum (Fig. 8a(iv)), a peak at 2689 cm<sup>-1</sup> is now observed and accompanied by the regeneration of BASs. The peak at 2689 cm<sup>-1</sup> could be assigned to the In-OD group considering that the peak position is higher than the BAS O-D group and extra-framework Al-OD group. The introduction of D<sub>2</sub>O again regenerates BASs, likely due to the hydrolysis of [InO]<sup>+</sup> and the formation of BASs. Subsequently, the introduction of D<sub>2</sub> and quantification of the number of consumed In-OD and BAS OD groups (Fig. 8(vii)) show reversibility between the reduced and oxidized states of the sample.

It follows that on a calcined sample, In<sub>2</sub>O<sub>3</sub> located on the external surface of the CHA zeolite was reduced and diffused into the micropores in the presence of H<sub>2</sub> at high temperature, displacing BASs and forming isolated In<sup>+</sup> sites. The O<sub>2</sub> treatment of the reduced In species leads to the formation of [InO]<sup>+</sup> and [In(OH)<sub>2</sub>]<sup>+</sup> and regeneration of BASs (Fig. 8b). H<sub>2</sub> pulses on the H<sub>2</sub>-O<sub>2</sub> treated In-CHA(11, 1.0) are consistent with the proposed oxidation state of isolated In<sup>+</sup> sites (Fig. S24†). The low ratio of formed H<sub>2</sub>O/consumed H<sub>2</sub> (~0.25) is interpreted as the result of the reaction of H<sub>2</sub>O—formed in the early portion of the catalyst bed—with [InO]<sup>+</sup> in the back end of the catalyst bed, a result consistent with the *in situ* FTIR spectra (Fig. 8a). Overall, the ratio of formed H<sub>2</sub>O/consumed H<sub>2</sub> during the entire experiment was estimated to be 1.1; that is, the main oxidized species was [InO]<sup>+</sup>, as supported by XRD that revealed no In<sub>2</sub>O<sub>3</sub>

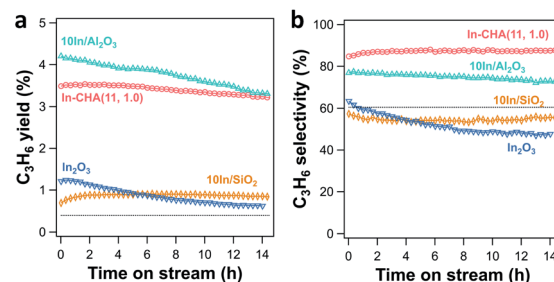


Fig. 9 (a) C<sub>3</sub>H<sub>6</sub> yield and (b) C<sub>3</sub>H<sub>6</sub> selectivity as a function of time on stream over In-CHA(11, 1.0), 10In/SiO<sub>2</sub>, 10In/Al<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub>. Reaction conditions: 600 °C, C<sub>3</sub>H<sub>8</sub> partial pressure 2.54 kPa with balancing N<sub>2</sub>, and space time 806 400 g<sub>Cat</sub> s mol<sub>C<sub>3</sub>H<sub>8</sub></sub><sup>-1</sup>. The propane conversions are below 6% in the rate measurements. The dotted line in the figure represents the C<sub>3</sub>H<sub>6</sub> yield (0.39%) in (a) and C<sub>3</sub>H<sub>6</sub> selectivity (60%) in (b) without a catalyst under the same conditions.

diffraction peaks detected on H<sub>2</sub>-O<sub>2</sub> treated In-CHA(11, 1.0) (Fig. S25†).

### Propane dehydrogenation mechanism on isolated In<sup>+</sup> sites

PDH catalytic rates and selectivity were measured on the reduced In-based catalyst. Calcined catalysts were reduced in 10 vol% H<sub>2</sub> for 30 min at 600 °C before the introduction of 2.54 kPa C<sub>3</sub>H<sub>8</sub> (balancing N<sub>2</sub>). At comparable conversion (<6%), In-CHA shows better stability than In<sub>2</sub>O<sub>3</sub>, 10In/SiO<sub>2</sub> and 10In/Al<sub>2</sub>O<sub>3</sub>. There is no significant decrease of the C<sub>3</sub>H<sub>6</sub> yield over 14 hours (Fig. 9a). A long-term test of the 10In/Al<sub>2</sub>O<sub>3</sub> sample (Fig. S26†) shows that the C<sub>3</sub>H<sub>6</sub> yield keeps decreasing within a time on stream of 65 hours, evidencing that indium supported on Al<sub>2</sub>O<sub>3</sub> exhibited poor stability for propane dehydrogenation. Isolated In<sup>+</sup> sites in In-CHA(11, 1.0) show good C<sub>3</sub>H<sub>6</sub> selectivity (~85%) at 600 °C (Fig. 9b), higher than the selectivity exhibited by the other samples. The higher reaction rates on 10In/Al<sub>2</sub>O<sub>3</sub> might be due to bare γ-Al<sub>2</sub>O<sub>3</sub> since it has been shown that (bare) γ-Al<sub>2</sub>O<sub>3</sub> catalyzes propane dehydrogenation.<sup>50</sup> A control experiment conducted on bare γ-Al<sub>2</sub>O<sub>3</sub> found that indeed this sample

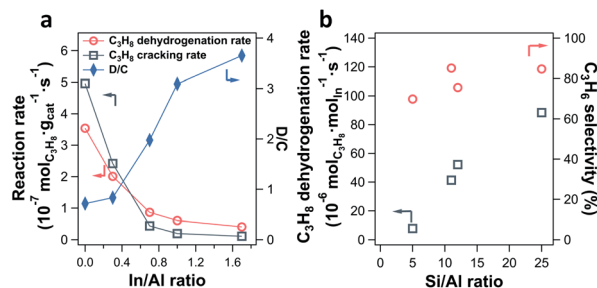


Fig. 10 (a) C<sub>3</sub>H<sub>8</sub> dehydrogenation rate and C<sub>3</sub>H<sub>8</sub> cracking rate as well as the ratio between the two (D/C) as a function of In/Al ratios on In-CHA (Si/Al = 12) catalysts. (b) C<sub>3</sub>H<sub>8</sub> dehydrogenation rate and C<sub>3</sub>H<sub>6</sub> selectivity as a function of Si/Al ratios on the In-CHA catalysts investigated (In/Al = 1). Reaction rates were collected at TOS = 21 min. Reaction conditions: 600 °C and C<sub>3</sub>H<sub>8</sub> partial pressure 2.54 kPa with balancing N<sub>2</sub>. The propane conversion is below 6% in the rate measurements.





displays higher catalytic rates and  $C_3H_6$  selectivity than 10In/ $Al_2O_3$  (Fig. S27†). Compared with the inert  $SiO_2$  support, 10In/ $SiO_2$  shows a higher  $C_3H_6$  yield and similar  $C_3H_6$  selectivity (~55%) (Fig. S28†). The reduction in the  $C_3H_6$  yield with time is attributed to the gradual reduction of  $In_2O_3$  to In(0), evidenced by the negligible reactivity exhibited by  $In_2O_3$  after being reduced for 8 hours (Fig. S29†).  $H_2O$  formation quantification and XRD measurements support that  $In_2O_3$  was completely reduced to In(0) after 8 hours of reduction (Fig. S29†). Considering the occurrence of the thermal cracking reaction of propane, we tested the empty tube for propane dehydrogenation ( $C_3H_8$  partial pressure 2.54 kPa with balancing  $N_2$ ). The  $C_3H_6$  yield and selectivity were 0.39% and 60%, respectively (see Fig. 9, dotted line). We then corrected the propane dehydrogenation reaction rate and cracking rate by subtracting the product derived from thermal cracking (see Fig. S30†). As expected, a small reduction in reaction rates was observed when considering the thermal cracking. The  $C_3H_6$  selectivity increased from 85% to 88% for the In-CHA catalyst, while the  $C_3H_6$  selectivity of 10In/ $Al_2O_3$  increased from 77% to 79%. For 10In/ $SiO_2$  and  $In_2O_3$  catalysts, there is no significant change in the  $C_3H_6$  selectivity when subtracting the thermal cracking products, which might result from the similar  $C_3H_6$  selectivity (~60%) of those catalysts with the thermal cracking reaction. Thus, we conclude that the CHA zeolite shows better stability and  $C_3H_6$  selectivity than indium on the other supports investigated.

We also examined the propane dehydrogenation reaction rate on the parent H-CHA (without indium); this catalyst shows higher catalytic rates than In-CHA(11, 1.0), and however, the rates decrease monotonically over time (Fig. S31†). In addition, the  $C_3H_6$  selectivity of H-CHA(11) is much lower, approximately 20% (Fig. S31†), than that on In-CHA(11, 1.0) (~85%). This observation confirms that In-CHA is stable and selective for the non-oxidative dehydrogenation of propane to propylene reaction while H-CHA favors propane cracking and has poor stability.

The impact of the In/Al ratio and Si/Al ratio of In-CHA catalysts on the PDH performance has also been examined (Fig. 10). With the increase of the In/Al ratio to 1.7 on the In-CHA (Si/Al = 12) catalyst, several interesting trends were observed: (1) the initial activity including  $C_3H_8$  dehydrogenation and  $C_3H_8$  cracking decreases; (2) the ratio between the  $C_3H_8$  dehydrogenation and  $C_3H_8$  cracking increases monotonically; (3) the catalyst exhibits better stability over 10 hours of testing (Fig. S32†). These observations are consistent with the results on H-CHA(11) and In-CHA(11, 1.0), showing that the addition of In could increase the  $C_3H_6$  selectivity by replacing BASs. The lower reactivity of In-CHA compared with H-CHA is due to the weak intrinsic activity of isolated  $In^+$  species than BASs. Interestingly, the  $C_3H_8$  dehydrogenation rate normalized to In loading declines as the Si/Al ratio decreases (Fig. 10b and S33†). In particular, the  $C_3H_8$  dehydrogenation rate decreased from 88  $\mu mol_{C_3H_8} mol_{In}^{-1} s^{-1}$  for In-CHA(25, 1.0) to 7.9  $\mu mol_{C_3H_8} mol_{In}^{-1} s^{-1}$  for In-CHA(5, 1.0).

Earlier we showed that for In/Al ratios  $\leq 1.0$ ,  $In_2O_3$  could be reduced to isolated  $In^+$  species, independent of Si/Al ratios. This

Table 2 The activation energies for propane dehydrogenation and cracking reactions on In-based and H-CHA catalysts

Sample	$C_3H_8$ dehydrogenation $E_{app}$ (kJ mol <sup>-1</sup> )	$C_3H_8$ cracking $E_{app}$ (kJ mol <sup>-1</sup> )
$In_2O_3$	143 ± 4.0	133 ± 3.8
10In/ $SiO_2$	179 ± 8.5	135 ± 7.4
10In/ $Al_2O_3$	69.5 ± 11.4	200 ± 3.9
In-CHA(11, 1.0)	94.3 ± 0.6	206 ± 11
H-CHA(11)	172 ± 2.7	130 ± 6.0
H-CHA(12)	190 ± 1.5	177 ± 1.8
In-CHA(12, 0.3)	188 ± 16	177 ± 12
In-CHA(12, 0.7)	149 ± 5.6	212 ± 3.0
In-CHA(12, 1.0)	109 ± 0.8	198 ± 1.5
In-CHA(12, 1.7)	125 ± 14	167 ± 19
H-CHA(25)	223 ± 2.0	206 ± 3.0
In-CHA(25, 1.0)	109 ± 1.5	265 ± 28
H-CHA(5)	180 ± 0.7	174 ± 3.2
In-CHA(5, 1.0)	187 ± 8.8	233 ± 6.4

excludes the possibility that a low concentration of  $In^+$  in In-CHA(5, 1.0) results in the decrease of In-normalized PDH rates. Considering that a cage of zeolite CHA contains more BASs as the Si/Al ratios decrease, it is more likely to form multi-nuclear  $In^+$  sites in one cage (or  $In^+-In^+$  sites) at low Si/Al ratios. These multi-nuclear species are detrimental to propane conversion and thus decrease the In-normalized rates compared with the case of one cage containing one  $In^+$  at high Si/Al ratios. The significant decrease of the micropore volume of In-CHA(5, 1.0) upon reduction compared with the reduced In-CHA(25, 1.0) catalyst (0.15 versus 0.29 cm<sup>3</sup> g<sup>-1</sup>, Table S1†) shows that In species occupy a good fraction of the micropore space on reduced In-CHA(5, 1.0). For H-CHA with varying Si/Al ratios, the BAS-normalized  $C_3H_8$  dehydrogenation rates are close to each other (approximately 280–370  $mol_{C_3H_8} mol_{BAS}^{-1} s^{-1}$ ) and  $C_3H_6$  selectivity is between 30% and 50% (Fig. S34 and S35†), showing similar  $C_3H_8$  dehydrogenation performance on CHA with varying BAS densities.

We prepared as a benchmark a PtSn/ $Al_2O_3$  catalyst (1%Pt and 2.6%Sn) using incipient wetness impregnation.<sup>51</sup> As shown in Fig. S36,† the PtSn/ $Al_2O_3$  catalyst showed a high initial  $C_3H_6$  yield (30%) and deactivated quickly within a time on stream of 5 hours, although the  $C_3H_6$  yield decreased slowly in the following 30 hours. The  $C_3H_6$  selectivity decreased from 97% to 91% within a time on stream of 35 hours. The deactivation trend is consistent with the results reported in ref. 51. We calculated the Pt normalized reaction rate (TOF<sub>Pt</sub>) based on the  $C_3H_6$  yield at TOS = 10 h (TOF<sub>Pt</sub> = 6.9  $mmol_{C_3H_6} mol_{Pt}^{-1} s^{-1}$ ). This value of TOF<sub>Pt</sub> is 78 times higher than TOF<sub>In</sub> determined on In-CHA(12, 1.0). Although  $In^+$  sites show a lower intrinsic reaction rate, it has better stability than PtSn/ $Al_2O_3$ .

Apparent activation energies ( $E_{app}$ ) for the PDH reaction on the reduced catalyst were estimated using an Arrhenius plot in the temperature range of 580–620 °C. On H-CHA(11), the  $E_{app}$  of the  $C_3H_8$  dehydrogenation and cracking reactions was 172 kJ mol<sup>-1</sup> and 130 kJ mol<sup>-1</sup> (Table 2). The lower  $E_{app}$  for  $C_3H_8$  cracking is typical for BASs since these sites favor cracking.<sup>41</sup>





The In-containing samples have, in contrast, much lower propane dehydrogenation  $E_{app}$  and higher propane cracking  $E_{app}$  (Table 2). The gradual decrease of  $E_{app}$  for  $C_3H_8$  dehydrogenation on In-CHA(12, 1.0) from 190 to 109 kJ mol<sup>-1</sup> as the In/Al ratio increases from 0 to 1.0 is consistent with the fact that In<sup>+</sup> dominates the reaction since the BAS density decreases, although it slightly increases as the In/Al ratio is increased to 1.7. A similar  $E_{app}$  for  $C_3H_8$  dehydrogenation on In-CHA(25, 1.0) was observed and an even higher  $E_{app}$  for  $C_3H_8$  dehydrogenation was found on In-CHA(5, 1.0), which evidenced that multi-nuclear In<sup>+</sup> sites in one cage (or In<sup>+</sup>-In<sup>+</sup> sites) are less effective than single sites.

In summary, isolated In<sup>+</sup> sites in the CHA zeolite favor dehydrogenation over cracking under all the conditions investigated. These observations are consistent with the high  $C_3H_6$  selectivity on the In-CHA(11, 1.0) catalyst. On In<sub>2</sub>O<sub>3</sub> and 10In/SiO<sub>2</sub> catalysts, both samples show higher  $E_{app}$  of  $C_3H_8$  dehydrogenation than the  $C_3H_8$  cracking reaction (Table 2), which is consistent with the lower  $C_3H_6$  selectivity (~50%) on the catalyst. Although lower  $E_{app}$  of  $C_3H_8$  dehydrogenation and higher  $C_3H_8$  cracking reaction were observed on 10In/Al<sub>2</sub>O<sub>3</sub>, the measured reaction rates were mainly the contribution of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support.

The turnover frequency (TOF) and pre-exponential factor were calculated over the In-CHA catalyst for propane dehydrogenation at 600 °C assuming that all the In is equally reactive. For In-CHA(11, 1.0), entropy changes of formation of the transition state for propane dehydrogenation are estimated based on transition state theory,<sup>18</sup> and determined to be -207 J mol<sup>-1</sup> K<sup>-1</sup> (Table S4†). The obtained entropy changes are larger than the values reported on H-[Fe]ZSM-5 (-155 J mol<sup>-1</sup> K<sup>-1</sup>) towards propane dehydrogenation.<sup>18</sup> This large negative entropy reflects that the transition state is geometrically constrained due to the small cage of the CHA zeolite. Similar trends are observed on In-CHA(25, 1.0) and In-CHA(12, 1.0); however, the quite distinct entropy changes of the transition state formation indicate the presence of a different active site on In-CHA(5, 1.0).

For In-CHA, the  $C_3H_8$  reaction order was 0.77 for dehydrogenation and 0.93 for cracking, close to the first order for both

reaction channels (Fig. 11a). In addition, the reaction order on H<sub>2</sub> is close to 0 (Fig. 11b); that is, H<sub>2</sub> is likely not part of the rate-determining step. These values are consistent with the reaction order values in In-CHA for ethane dehydrogenation.<sup>33</sup> These reaction orders can be rationalized by the following mechanisms: the propane C-H bond is initially dissociated through an oxidative addition process by isolated In<sup>+</sup> to form [HIn(III)-C<sub>3</sub>H<sub>7</sub>]<sup>+</sup> species. This step is followed by H-beta elimination with the formation of a metastable [H<sub>2</sub>In(III)-C<sub>3</sub>H<sub>6</sub>]<sup>+</sup> intermediate. The catalytic cycle is closed by the desorption of C<sub>3</sub>H<sub>6</sub>, and the reductive elimination of H<sub>2</sub> to form In<sup>+</sup> (Scheme 1). The reaction order of ~1 for  $C_3H_8$  and ~0 for H<sub>2</sub> point to the first step as the rate-determining step.

TG analysis of the spent catalyst illustrates the high stability of the In-CHA(11, 1.0) catalyst. After a time-on-stream of 14 hours, the samples show only a small amount of coke formation (~2.4%, Fig. S37†), a value lower than that on the H-CHA(11) catalyst, confirming that the deactivation of the H-CHA catalyst is mainly due to the formation of coke and that an isolated In<sup>+</sup> site is less prone to coke formation reactions. There may be a steric contribution to catalysis on In-CHA compared with H-CHA, considering that the available micropore volume on reduced In-CHA is lower than that on the parent H-CHA (Table S1†). Another possibility is that propylene adsorbs more strongly on H<sup>+</sup> sites than In<sup>+</sup> sites (*i.e.*, has higher heats of adsorption). As shown in Fig. S38,† upon introducing C<sub>3</sub>H<sub>6</sub> on the H-CHA catalyst surface, significant consumption of BASs (3575 cm<sup>-1</sup>) is observed. Upon evacuation of C<sub>3</sub>H<sub>6</sub>, a strong signal associated with hydrocarbon species centered at 3055 cm<sup>-1</sup> is detected,<sup>36</sup> showing that C<sub>3</sub>H<sub>6</sub> has a strong interaction with BASs and forms stable hydrocarbon species, which could lead to coke formation. No stable hydrocarbon species are observed when introducing C<sub>3</sub>H<sub>8</sub> and C<sub>3</sub>H<sub>6</sub> on the reduced In-CHA(12, 1.0), showing that In<sup>+</sup> has a weak interaction with C<sub>3</sub>H<sub>8</sub> and C<sub>3</sub>H<sub>6</sub>, which is also a reason for the low formation rate of coke. XRD measurements on the spent catalyst confirmed that no significant structural change occurred on the CHA catalysts, or on the reduced samples (Fig. S39†). It is worth noting that the relative intensities between the diffraction peaks at ~9° and ~21° decreased on In-CHA samples compared with H-CHA, suggesting that the formed extra-framework In<sup>+</sup> sites are stable

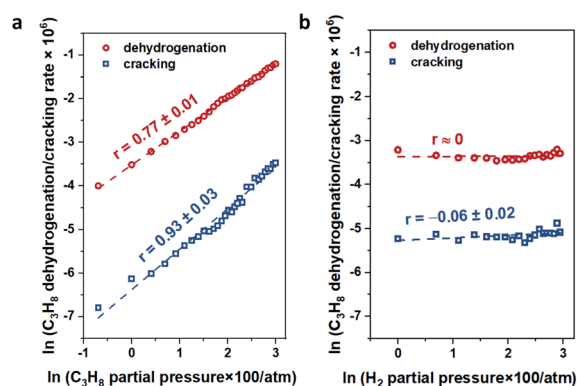
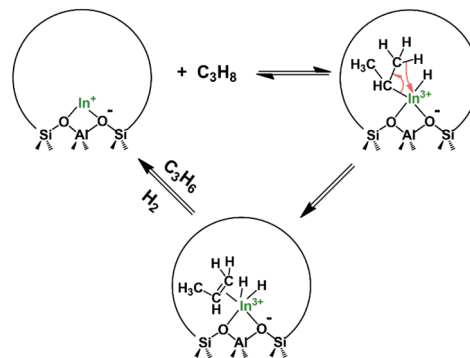


Fig. 11 The dependence of propane dehydrogenation and cracking reactions on (a) propane partial pressure and (b) H<sub>2</sub> partial pressure over the In-CHA(11, 1.0) catalyst at 600 °C.



Scheme 1 Schematic of proposed mechanisms for PDH on isolated In<sup>+</sup> sites.



after the propane dehydrogenation reaction. On the spent  $\text{In}_2\text{O}_3$  sample, there is an overall increase in the sample weight during TGA, attributed to the oxidation of  $\text{In}(0)$  to indium oxide. This is consistent with the results presented above showing that  $\text{In}(0)$  is present on the reduced  $\text{In}_2\text{O}_3$  catalyst. The slight decrease of the weight on  $10\text{In}/\text{SiO}_2$  and  $10\text{In}/\text{Al}_2\text{O}_3$  results from the combined effect of the two processes: oxidation of  $\text{In}(0)$  to indium oxide and removal of formed coke.

Main-group compounds containing a group 13 metal (I) compound ( $\text{M} = \text{Al}, \text{Ga}, \text{In}$ ) have been prepared for oxidative addition and reductive elimination reactions of strong single bonds such as  $\text{X-H}$   $\sigma$  bonds ( $\text{X} = \text{H}, \text{C}, \text{Si}, \text{P}, \text{etc.}$ ). These are key steps in catalytic cycles and are frequently observed in organometallic transition-metal chemistry.<sup>52</sup> These highly reactive compounds with low oxidation states have been shown to possess high-energy lone pairs and available empty (usually  $\pi$ -antibonding) orbitals, thereby mimicking the state of electrons observed in transition-metal compounds. For instance, Seifert *et al.*<sup>53</sup> found that the gallium(i) complex  $[\text{Ga}\{\text{N}(\text{dipp})\text{CMe}_2\text{CH}\}]$  ( $\text{dipp} = 2,6$ -diisopropylphenyl) undergoes facile oxidative addition reactions with various *element-hydrogen* bonds at relatively low temperature ( $-78$  to  $25$  °C). Beachley *et al.*<sup>54</sup> reported that organoindium compounds  $\text{NaIn}(\text{CH}_2\text{-SiMe}_3)_2$  with indium in the +1 oxidation state could be prepared from  $\text{In}(\text{CH}_2\text{SiMe}_3)_3$  and  $\text{NaH}$  *via* a reductive elimination reaction with  $\text{Si}(\text{CH}_3)_4$  as another product. These examples suggest that main-group compounds with low oxidation states can catalyze C-H bond scission *via* oxidative addition and reductive elimination processes. In this case,  $\text{In}^+$  in the CHA zeolite could be regarded as an analogue of an  $\text{In}(\text{i})$  molecular complex, which catalyzes propane dehydrogenation first through the oxidative addition of propane to form  $[\text{HIn}(\text{iii})\text{-C}_3\text{H}_7]$  species, and then proceeds *via* H-beta elimination with the formation of an  $[\text{H}_2\text{In}(\text{iii})\text{-C}_3\text{H}_6]$  intermediate, and the cycle is closed by the desorption of  $\text{C}_3\text{H}_6$  and the reductive elimination of  $\text{H}_2$  to form  $\text{In}^+$  (Scheme 1). Our findings are a good example of the connection between the chemistry of metals in extra-framework positions and the molecular chemistry of main-group elements like  $\text{In}$  and  $\text{Ga}$ . This line of thought may be a fruitful avenue to identify novel catalytic applications of these materials and other main-group elements supported on acidic zeolites.

## Conclusions

This report shows that CHA zeolites stabilize  $\text{In}$  in the +1 oxidation state as isolated species in extra-framework positions, independent of  $\text{In}/\text{Al}$  ratios and  $\text{Si}/\text{Al}$  ratios. In contrast,  $\text{In}/\text{SiO}_2$ ,  $\text{In}/\text{Al}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  form substantial amounts of  $\text{In}(0)$  upon reduction in  $\text{H}_2$ .  $\text{In}$ -CHA shows quantitative and reproducible redox cycles by sequentially exposing the sample to sets of  $\text{O}_2$  and  $\text{H}_2$  pulses producing first mixtures of  $\text{InO}^+$  and  $(\text{In}(\text{OH})_2)^+$  and then  $\text{In}^+$  upon reduction.  $\text{In}^+$  in CHA zeolites catalyzes propane dehydrogenation with a  $\text{C}_3\text{H}_6$  selectivity of  $\sim 85\%$ , with minor propane cracking to methane and ethylene. Coke formation is minimal ( $<2.5\%$  w/w) over a period of 14 h. The dehydrogenation selectivity over  $\text{In}$ -CHA is much higher than the selectivity observed over  $\text{In}/\text{SiO}_2$ ,  $\text{In}/\text{Al}_2\text{O}_3$  and bulk  $\text{In}_2\text{O}_3$ .

The mechanism of the propane dehydrogenation reaction seems to proceed through a sequence of oxidative addition, beta-H elimination, and reductive elimination of a (postulated) dihydride indium intermediate, based on the reaction rate orders with respect to propane and hydrogen obtained at low conversions. There are clear analogies between the observed chemistry of  $\text{In}^+$  in CHA zeolite and  $\text{In}^+$  organometallic complexes.

## Data availability

All data needed to evaluate the conclusions in the paper are present within the article or in the ESI file.† Additional data related to this paper may be requested from the authors.

## Author contributions

Y. Y. and R. F. L. conceived the research project. Y. Y. conducted the experiments. Y. Y. and R. F. L. analyzed data and wrote the paper. All authors have given approval of the final version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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