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Mechanism and Kinetics of Propane and n-Butane Dehydrogenation over Isolated and Nested $\equiv\text{SiOZn-OH}$ Sites Grafted onto Silanol Nests of Dealuminated Beta Zeolite

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Abstract

Zn Lewis acid centers were grafted into the silanol nest created by dealumination of H-Beta zeolite (DeAlBEA). The resulting material was characterized and investigated for propane dehydrogenation to propene and n-butane dehydrogenation to 1,3-butadiene (1,3-BD). For Zn/Al molar ratios (Al is the molar amount in H-BEA) below 0.12, Zn sites are present as isolated ($\equiv\text{SiOZn-OH}$) species but for Zn/Al ratios between 0.12 to 0.60, the $\equiv\text{SiOZn-OH}$ species form nests in which enhanced electron-transfer between Zn and O atoms of neighboring $\equiv\text{SiOZn-OH}$ group and H-bonding interaction between adjacent Zn-OH groups occur. The turnover frequency (TOF) for both propane and n-butane dehydrogenation are virtually identical for Zn-DeAlBEA for Zn/Al < 0.12, and then increases almost linearly with increasing Zn/Al ratio from 0.12 to 0.36, indicating the superior activity of Zn atoms in $\equiv\text{SiOZn-OH}$ nests. In the case of 1-butene dehydrogenation, identical activity is observed for both isolated and nested $\equiv\text{SiOZn-OH}$ sites. The kinetics of these three reactions were investigated to clarify the difference in activity. The rate coefficient for the forward reaction (dehydrogenation) was found to 173 mol propene/(mol Zn sites $\cdot$ bar $\cdot$ h) at 773 K over $\equiv\text{SiOZn-OH}$ nests and that for the forward n-butane dehydrogenation was found to be 1193 mol butene/(mol Zn sites $\cdot$ bar $\cdot$ h) at 823 K, value that is significantly higher than those for most other supported non-noble metal catalysts. Regeneration experiments for propane and n-butane dehydrogenation over 0.60Zn-DeAlBEA suggest a good stability of Zn atom in $\equiv\text{SiOZn-OH}$ nests.

Keywords: propane dehydrogenation, n-butane dehydrogenation, isolated Zn site, nested Zn site, dealuminated Beta zeolite, kinetics

Introduction

Propene and 1,3-butadiene (1,3-BD) are two of the most important chemical intermediates produced industrially.¹ Propene is used for the production of products such as polypropylene, propylene oxide, acrylic acid, acrylonitrile, etc.,²⁻⁷ whereas, 1,3-BD is used primarily for the production of synthetic rubbers and other polymers.^{8, 9} Historically, propene has been produced by steam cracking and fluid catalytic cracking (FCC) of petroleum. By contrast, 95% of global 1,3-BD production has been obtained via extractive distillation of C₄ fractions formed as by-products of naphtha steam cracking.¹⁰ Because of the recent availability of light alkanes in the condensable fraction of natural gas and naphtha, growing attention has focused on direct dehydrogenation of light alkanes to produce alkenes and diolefins. This trend is also motivated by the attractive price gap between alkanes and alkenes.

While Pt- and CrO_x-based catalysts have been used traditionally for light alkane dehydrogenation, Pt is expensive and chromia is toxic and deactivates rapidly, requiring frequent regeneration.⁶ Driven by increasing economic interest in light alkane dehydrogenation, various non-noble metal and metal oxides (e.g., Zn, Sn, Co, Ga, Fe, In, V, etc.) have been explored as dehydrogenation catalysts.^{4, 11-21} Among them, Zn-based catalysts show promise because of the low cost of Zn and its high catalytic activity for alkane dehydrogenation.²²⁻²⁵ Bulk ZnO is not active for alkanes dehydrogenation,^{22, 25, 26} and at high temperatures where dehydrogenation is favorable reduces to form liquid metallic zinc (mp 693 K²⁷), which can sublime. For this reason, significant efforts have been undertaken to explore the activity and selectivity of supported Zn catalysts synthesized by different techniques, e.g., ion exchange (IE), incipient wetness impregnation (IWI), chemical vapor deposition (CVD) on silica and zeolite supports.^{22, 23, 25, 26, 28-37}

One approach for dispersing Zn is cation exchange of Zn²⁺ for protons in protonated zeolites. Chemical vapor deposition (CVD) of dimethylzinc has been used to produce Zn/H-ZSM-5. This catalyst exhibits good activity for propane dehydroaromatization. Characterization of this material showed a heterogeneous distribution of extra-

framework Zn species and the authors of this study concluded that multinuclear oxygenated zinc clusters and bulk zinc oxide aggregates are more active than isolated Zn^{2+} cations.³⁶ Zn modified HZSM-5 and HY zeolites have been synthesized by atomic layer deposition (ALD) using diethylzinc as the precursor, to produce isolated $\text{Zn}(\text{OH})^+$ species that are reported to be the active sites for propane to propene and aromatics.³⁸ Zn/H-ZSM-5, prepared by ion exchange produces Zn^{2+} cations interacting with two Al atoms ($-\text{O}-\text{Zn}^{2+}-\text{O}-$), has also been found to be active for alkane dehydrogenation.³⁰ More recently, we have reported the preparation of Zn/H-MFI by solid-state ion exchange.³⁹ This work showed that $[\text{ZnH}]^+$ cations formed by H_2 pretreatment of the as-prepared catalyst readily transform to bridging Zn^{2+} cations during propane dehydrogenation, which exhibit higher dehydrogenation activity and propene selectivity than $[\text{ZnH}]^+$ cations. A systematic investigation of Zn speciation in Zn/H-ZSM-5 and the activity of this catalyst for propane dehydrogenation concludes that isolated Zn^{2+} preferentially formed over pairs of Al sites for low Zn loadings, and that $[\text{Zn}-\text{O}-\text{Zn}]^{2+}$ and $[\text{ZnOH}]^+$ species, and then ZnO_x clusters are formed as the Zn loading is increased. Consistent with previous findings, the authors of this work find that $[\text{Zn}-\text{O}-\text{Zn}]^{2+}$ and $[\text{ZnOH}]^+$ species exhibit high dehydrogenation activity.⁴⁰ It should be noted that exchange of Zn^{2+} cations for H^+ cations in the proton form of a zeolite always leaves some unexchanged Brønsted acid sites. These sites exhibit both dehydrogenation and cracking activity, and promote the alkene oligomerization, isomerization, and aromatization, thereby decreasing the olefin selectivity observed during light alkane dehydrogenation.²² For this reason it is desirable to consider dispersing Zn on supports that are free of Brønsted acid sites.

Zinc has been grafted onto SiO_2 and siliceous zeolites, such as Silicalite-1 and dealuminated Beta (DeAlBEA) zeolite, which are free of Brønsted acid sites. Zn^{2+} cations have been grafted onto SiO_2 by strong electrostatic adsorption.²² These sites exhibit >95% selectivity to propene for propane dehydrogenation at 823 K. Isolated Zn sites are proposed to be tetrahedrally coordination with three $\text{Si}-\text{O}-\text{Zn}$ surface covalent bonds and one dative bond to a water molecule. At elevated temperature, loss of one

Zn–O bond was observed, forming a coordinatively unsaturated, three-coordinated Zn^{2+} site capable of catalyzing both propane dehydrogenation and propene hydrogenation. A novel synthetic strategy has been reported recently for the preparation of ZnO-silicalite-1. The method begins with the placement of a layer of ZnO placed upstream of a layer of Silicalite-1. When this mixture is heated in a reducing atmosphere, Zn is transferred to OH groups associated with defects in the lattice of Silicalite-1 as volatile Zn^0 and binuclear ZnOx .⁴¹

In a separate study, ALD was used to create alkyl zinc and zinc oxide-type sites on silica.²⁵ Tricoordinated ethyl zinc-silica sites exhibited higher activity compared to tetracoordinated zinc oxide-type centers. However, the reported propane dehydrogenation activity for these two Zn/SiO₂ catalysts was $<1 \text{ h}^{-1}$ in the presence of 2.5–3 kPa of propane at 823 K with a low propane conversion $<10\%$.²² Zn nanoparticles confined in Silicalite-1 zeolite have been reported to exhibit almost no activity for propane dehydrogenation.² However, small ZnO nanoclusters supported on DeAlBEA, with an optimal loading 10 wt% Zn has been reported to give an initial net propane dehydrogenation activity of 2.7 h^{-1} , and a propene selectivity of about 93% at 5.07 kPa of propane and 873 K.²⁴

The obvious differences in catalytic performance of silica-supported Zn catalysts discussed above demonstrate the need for a more comprehensive investigation of the chemical structure of grafted Zn sites and the influence of their local environment on their catalytic performance for alkane dehydrogenation. In this work, Zn Lewis acid sites with an open site structure ($\equiv\text{SiOZn-OH}$) were grafted onto the silanol nests of DeAlBEA and tested for both propane dehydrogenation to propene and n-butane dehydrogenation to butene isomers and 1,3-BD. Isolated and nested $\equiv\text{SiOZn-OH}$ species were generated and systematically characterized as a function of Zn/Al molar ratio, where Al is the molar amount of Al in the parent H-BEA. An important finding is that the dehydrogenation activity per Zn atom for both propane and n-butane are both enhanced significantly when $\equiv\text{SiOZn-OH}$ sites are nested. It is notable that the activity of 1-butene dehydrogenation to 1,3-BD, which follows the dehydrogenation of n-

butane, is identical for both isolated and nested $\equiv\text{SiOZn-OH}$ site. As a complement to these findings, detailed studies were carried out of the mechanism and kinetics of propane dehydrogenation to propene, n-butane dehydrogenation to butenes, and 1-butene dehydrogenation to 1,3-BD. Moreover, the activity and regenerability of Zn sites for propane and n-butane dehydrogenation were examined over 0.6Zn-DeAlBEA at 823 K. For both processes, 0.6Zn-DeAlBEA could be regenerated three times without significant loss of activity.

Results and Discussion

Catalyst characterization

The dealumination of H-BEA zeolite was characterized by IR spectroscopy. IR spectra of surface hydroxyl groups taken before and after dealumination of H-BEA (Figure S1A) demonstrate that all Al-related OH groups,⁴² including bands at 3606 cm^{-1} (Brønsted acid O–H groups) and at 3660 and 3780 cm^{-1} (Al–OH groups), disappeared after dealumination. Concurrently, the intensity of the bands for internal silanol groups at 3732 cm^{-1} increased and a broad, intense band centered around 3520 cm^{-1} characteristic silanol nests appeared.^{43, 44} IR spectra of adsorbed pyridine (Figure S1B) show that the bands for pyridine interacting with Brønsted acid sites (1545 and 1637 cm^{-1}), Lewis acid sites (1620 and 1455 cm^{-1}), and the combination of Brønsted and Lewis acid sites (1490 cm^{-1}) associated with H-BEA disappear upon dealumination. In the place of these features, two new bands appear at 1596 and 1445 cm^{-1} that are accompanied by two negative peaks centered at 3732 and 3500 cm^{-1} , indicating that pyridine interacts with the hydrogen- (H-) bonded Si-OH group,^{43, 45} further confirmed the absorption of pyridine on the H-bonded silanol. XRD patterns for H-BEA and DeAlBEA (Figure S2A) show that the zeolite structure is retained after dealumination. Taken together, these observations indicate that silanol nests are created upon dealumination of H-BEA.

Zn species were introduced into DeAlBEA by aqueous impregnation. ICP analysis (Figure S2B) indicates that almost all of the Zn in the solution used for impregnation is

grafted onto the support. IR spectra of 0.12Zn-DeAlBEA and DeAlBEA shown in Figure 1A demonstrate that after introduction of Zn, the band for silanol nests centered at around 3500 cm^{-1} decreased significantly in intensity, indicating the consumption of silanol groups and disruption of the H-bonding among them in the silanol nests. Consistent with this interpretation, the signals for H-bonded pyridine at 1596 and 1445 cm^{-1} also decrease (Figure 1B) by $\sim 82\%$ when the Zn/Al ratio is raised from 0 to 0.12. Moreover, two new bands appear at 1610 cm^{-1} and 1450 cm^{-1} that are ascribed to pyridine interacting with Zn Lewis acid sites;⁴³ the intensity of these peaks increases with increasing Zn/Al ratio (Figure 1B). The XRD patterns of Zn-DeAlBEA (Figure S2A) show that the zeolite structure is retained after introduction of Zn, irrespective of the Zn/Al ratio, without the appearance of characteristic peaks for bulk ZnO_x . Measurements of BET surface area by N_2 adsorption show that all of the samples have surface areas of $300\text{-}320\text{ m}^2\text{ g}^{-1}$ (Table S1).

Quantitative analysis of the IR band at 1610 cm^{-1} for adsorbed pyridine shows that the peak area increases linearly with Zn/Al ratio up to a ratio of about 0.36 (Figure 1C), suggesting the generation of isolated Zn Lewis acid sites in this range. Beyond this value, the peak area further increases with Zn/Al ratio but at a lower rate. We propose that this trend may be associated with the generation of ZnO_x oligomers containing Zn-O-Zn bonds for Zn/Al ratios higher than 0.36; however, no direct evidence for Zn-O-Zn bonds could be obtained from UV-vis, XPS and XAS spectra (vide infra).

For BEA zeolite with a Si/Al ratio of 14, it has been reported that approximately half of the Al sites are in pairs.⁴⁶ More recently, Tabor et al. have reported that both Al pairs and “close unpaired Al” atoms are common for BEA zeolite, and that the fraction of Al in next-nearest neighbors (NNN) and next-next-nearest neighbors (NNNN) pairs varies from 40% to 65% in BEA with $\text{Si/Al} < 18$.⁴⁵ Therefore, creation of neighboring silanol nests can be expected upon removal of proximate Al atoms.⁴⁶⁻⁴⁸ As a consequence, neighboring Zn sites are expected to be generated when Zn atoms are grafted into these proximate silanol nests.

It should be noted that, as the Zn/Al ratio increases from 0.12 to 0.36, the intensity

of the band at 3500 and 1596 cm^{-1} (Figure 1D) exhibit very limited intensity decrease, even though the bands at 1610 and 1450 cm^{-1} for pyridine interaction with Lewis acidic Zn^{2+} cations in $\equiv\text{SiOZn-OH}$ groups increase in intensity for Zn/Al ratios up to 0.36 (see Figure 1C), which clearly indicates increasing grafting of Zn^{2+} into DeAlBEA. This is contrary to what would be expected - a decrease as a consequence of consumption of H-bonded $\equiv\text{Si-OH}$ groups. As mentioned above, the band at 1596 cm^{-1} is attributable to the interaction of pyridine with H-bonded silanol groups. A plausible explanation for this observation is that the newly grafted Zn sites are present as Zn-OH groups, which H-bond with each other or with residual Si-OH groups, leading to the unchanged and even slight intensification of the band at 1596 cm^{-1} . Further evidence regarding to the generation of Zn-OH group is given below.

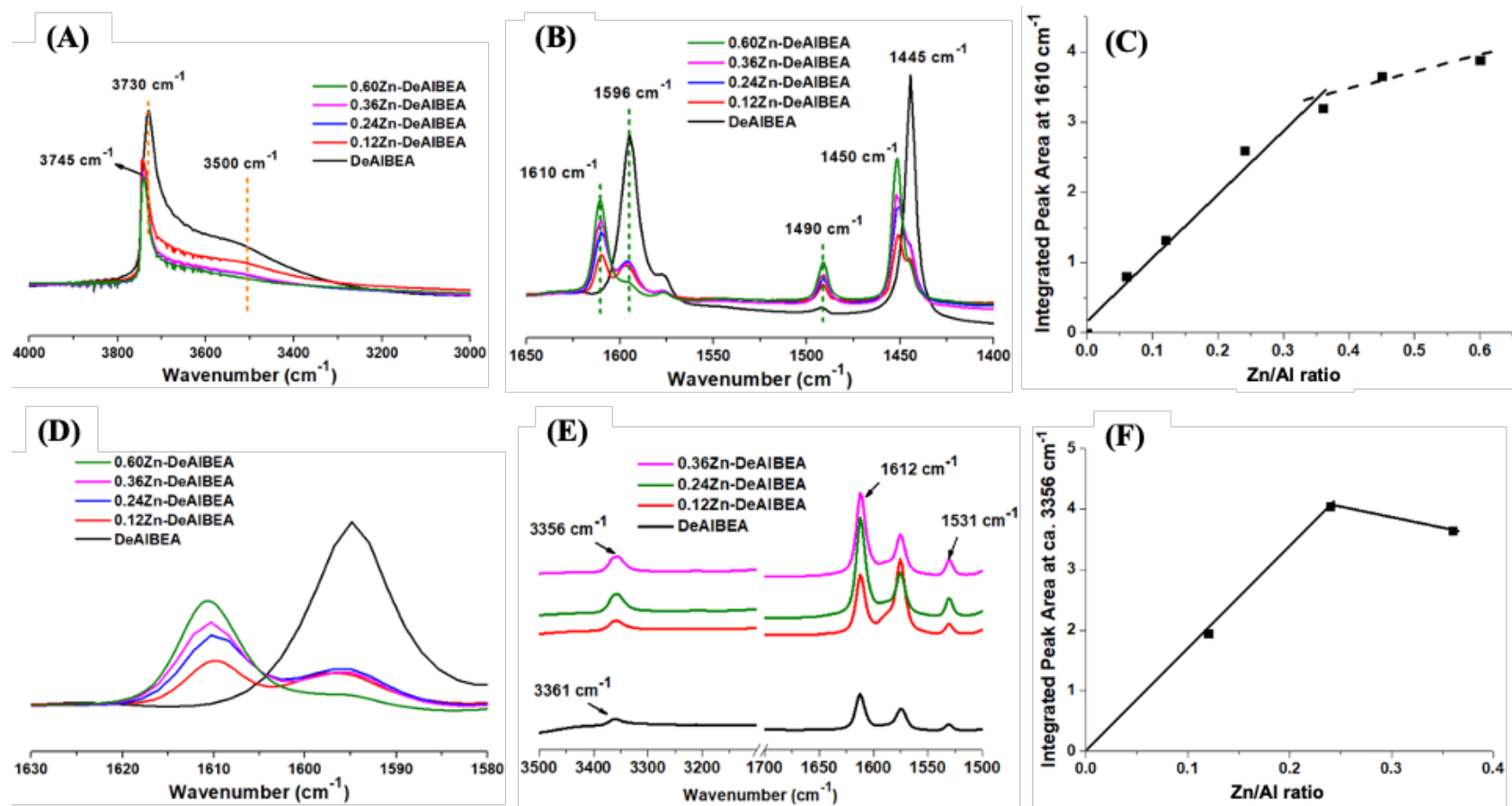


Figure 1. (A) IR spectra for the hydroxyl stretching region and (B) IR spectra following pyridine adsorption on DeAlBEA and Zn-DeAlBEA with varying Zn/Al ratios. (C) Plots of the integrated area for IR band at 1610 cm^{-1} for adsorbed pyridine versus the Zn/Al ratio. (D) Enlarged part of IR spectra for pyridine adsorbed on Zn-DeAlBEA. (E) IR spectra of 2,6-di-tert-butyl pyridine (DTBPy) adsorbed on DeAlBEA and Zn-DeAlBEA with varying Zn/Al ratios, and (F) dependence of the integrated area for the IR bands at 3356 cm^{-1} on Zn/Al ratio.

In contrast to pyridine, more basic 2,6-di-tert-butyl pyridine (DTBPy) can accept protons from weakly acidic OH groups associated with Lewis acidic metal sites (M-OH groups). Previous studies of Zr-BEA^{49,50} and Al-BEA⁵¹ zeolites have demonstrated that DTBPy could easily penetrate into the pores network of 12-MR Beta zeolite, enabling M-OH groups to be probed by IR spectroscopy of adsorbed DTBPy. To get insights into the chemical structure of grafted Zn Lewis acid site, IR spectra were obtained for DTBPy adsorbed on Zn/DeAlBEA with Zn/Al ratios of 0.12 to 0.36. As illustrated in Figure 1E, three bands are observed at 1612, 1531 and 3356 cm⁻¹ attributable to protonated DTBPy.⁴⁹⁻⁵¹ The IR spectrum of adsorbed DTBPy also exhibits bands for relatively weak protonated DTBPy interacting with H-bonded silanol nests.⁴¹ The band at ca. 3356 cm⁻¹ is characteristic of $\nu(\text{N-H}^+)$ vibrations and is generally used for determining acid sites concentrations.⁴⁹⁻⁵¹ Figure 1F shows that the integrated area of the band at 3356 cm⁻¹ increases linearly as the Zn/Al ratio increases from 0.12 to 0.24, which is another indicator for the presence of isolated Zn sites. More importantly, the observation of an IR band at 3356 cm⁻¹ and its linear dependence with Zn content provides additional support for the conclusion that the grafted Zn species are present as $\equiv\text{SiOZn-OH}$ groups.

When the Zn/Al ratio is further increased to 0.36, no further increase in the intensity of the band at 3356 cm⁻¹ is observed, which appears to be contradictory with that observed by IR spectroscopy of adsorbed pyridine seen in Figure 1C. Considering the much larger kinetic diameter of DTBPy vs pyridine, this observation could be due to serious steric hindrance when DTBPy interacts with $\equiv\text{SiOZn-OH}$ sites grafted in proximate silanol nests^{52,53}.

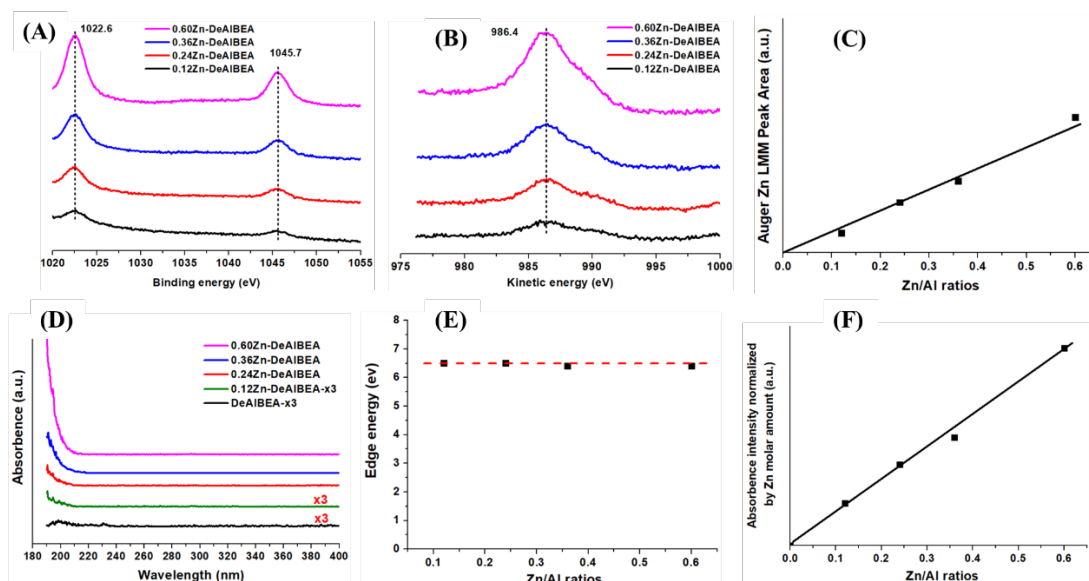


Figure 2. (A) XPS spectra of the Zn 2p and (B) Zn LMM core levels of Zn-DeAlBEA samples with different Zn/Al ratios. (C) Integrated Auger Zn LMM signals. (D) UV-vis spectra of Zn-DeAlBEA with different Zn/Al ratios. (E) Zn edge energy for Zn-DeAlBEA. (F) UV-vis absorbance intensity normalized per Zn versus Zn/Al ratio of Zn-DeAlBEA.

Figure 2A presents XPS spectra of Zn-DeAlBEA with Zn/Al ratio ranging from 0.12 to 0.60. The Zn 2p_{3/2} and Zn 2p_{1/2} binding energies (BE) are 1022.6 and 1045.7 eV, respectively, independent of the Zn/Al ratio. The spin-orbit splitting of Zn 2p peaks of 23.1 eV together with the XANES results shown below suggest that all of the Zn is in the 2+ oxidation state.⁵⁴ We note that, the BEs for Zn cations in Zn-DeAlBEA are higher than that for ZnO_x nanoparticles (~5 nm in size) supported on DeAlBEA, 1021.6 and 1044.9 eV.²⁴ Since the electronegativity of Zn is lower than that of Si atom, Zn in Zn-O-Si bonds would be more positively charged than in Zn-O-Zn bonds, resulting in a shift towards higher BEs. Consequently, the observed high BE for Zn in Zn-DeAlBEA is consistent with the absence of Zn-O-Zn bonds, suggesting a high dispersion of Zn in isolated species. The Auger Zn LMM spectra exhibit a peak at 986.4 eV for all samples examined (Figure 2B). Accordingly, the Auger parameter ($\alpha = E_{B,2p_{3/2}} + E_{k,LMM}$) of Zn-DeAlBEA is 2009.0 eV, 1.25 eV lower than that of pure ZnO (2010.25 eV), which further confirms the formation of Si-O-Zn bonds rather than Zn-O-Zn bonds.⁵⁵ Furthermore, the intensity of Auger Zn LMM signals increase linearly as the Zn/Al ratio increases from 0.12 to 0.60. The absence of a change in the position of this Auger peak

as well as the linear increase in its intensity with Zn/Al ratio are also consistent with the generation of isolated Zn sites for Zn/Al ratios between 0.12 and 0.60. Moreover, the absence of changes in peak position and shape suggests that neither the oxidation state nor the aggregation of Zn into Zn-O-Zn species occur. Thus, the findings obtained from XPS are consistent with the IR results for adsorbed pyridine discussed above. In summary, the XPS data indicate that most of the Zn atoms are grafted to the zeolite framework via Zn-O-Si bonds.

Figure 2D presents UV-vis spectra for DeAlBEA and Zn-DeAlBEA. DeAlBEA exhibits a broad absorption peak centered at ca. 200 nm, attributable to the presence of $\equiv\text{Si-OH}$ groups.^{56, 57} After grafting Zn, this absorption peak loses intensity, due to the consumption of $\equiv\text{Si-OH}$ groups, and a new sharp band appears at around 195 nm, which can be assigned to charge transfer from lattice O^{2-} in zeolite framework to isolated Zn sites.^{58, 59} As the Zn/Al ratio increases, the maximum in this UV-vis absorbance increases. These observations further confirming the grafting of Zn species onto the zeolite framework. For $\text{Zn/Al} \leq 0.60$, an absorption band near 368 nm is not observed, indicating the absence of Zn-O-Zn bond ascribed to macrocrystalline ZnO_x oligomers or nanoparticles.²⁴ We note as well that the photon absorption energies attributable to ligand-to-metal charge transfer (LMCT) from O to an isolated Zn(II) are estimated to be around 6.4-6.5 eV for all Zn-DeAlBEA samples (Figure 2E, Figure S3). This value is much higher than that for bulk ZnO, 3.15 eV,⁶⁰ indicating that Zn on DeAlBEA exists predominantly as isolated sites with low connectivity in strong agreement with the XPS result discussed above.

Consistent with the occurrence of weak interactions between neighboring Zn cations deduced from IR spectra of adsorbed pyridine and DTBPy, the intensity of UV-vis absorbance normalized per Zn atom shows a linear dependence on the Zn/Al ratio (Figure 2F). The observed linear increase in the intensity of UV-vis feature per Zn atom with Zn/Al ratio is attributed to enhanced ligand-to-metal charge transfer due to $\equiv\text{SiOZn}(\text{OH}) \rightarrow \text{Zn}$ interactions. Similar enhancement in the LMCT characteristics due to the presence of electron-rich ligands having functional groups such as hydroxyl

groups has been reported for Ti.⁶¹ Further direct evidence characterizing the interaction between neighboring Zn sites is provided by the EXAFS data for Zn-DeAlBEA (Zn/Al = 0.36) taken from Ref. ⁶² and shown in Table 1.

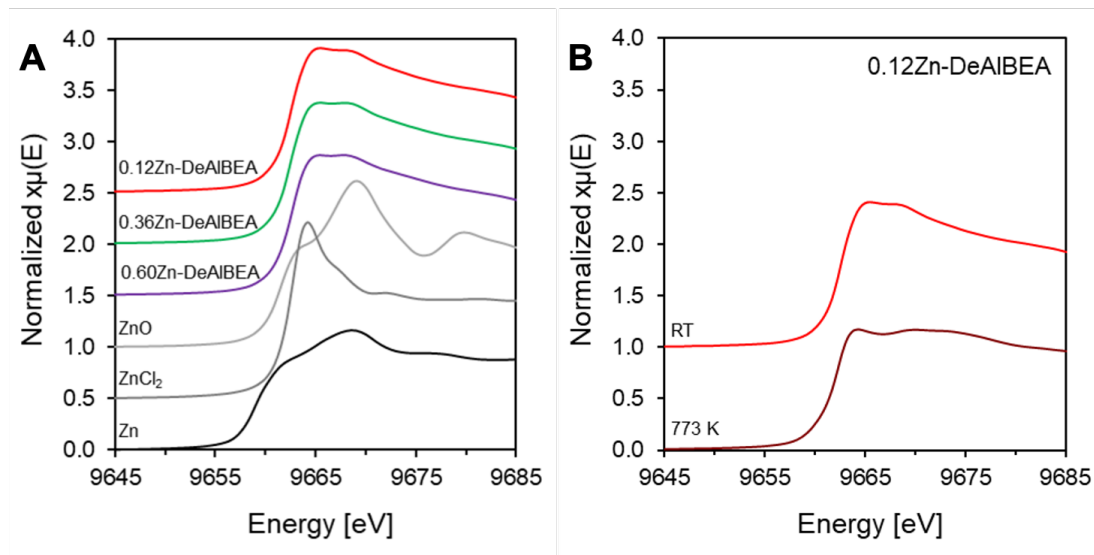


Figure 3. Normalized Zn K-edge X-ray absorption near-edge spectra (XANES) of Zn-DeAlBEA and Zn standards. a) XANES spectra of 0.12Zn-DeAlBEA, 0.36Zn-DeAlBEA, and 0.60Zn-DeAlBEA at ambient temperature in He. XANES spectra of ZnO, ZnCl₂, and Zn metal standards at ambient temperature in air are also shown. b) XANES spectra of 12Zn-DeAlBEA at ambient temperature in He, and at 773 K in He. The spectra are offset for clarity.

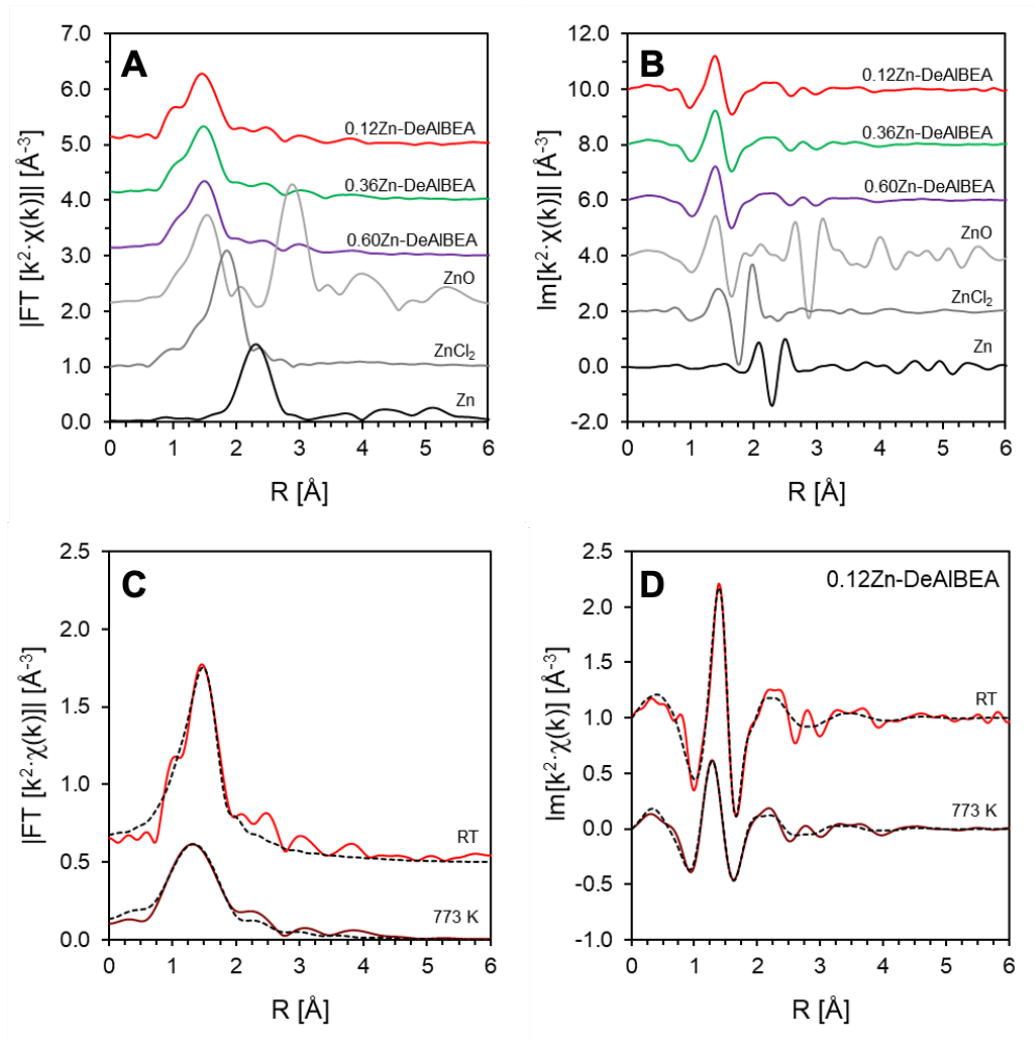


Figure 4. (A) Real and (B) imaginary components of the Fourier-transformed k^2 -weighted extended X-ray absorption fine structure spectra (EXAFS) of 0.12Zn-DeAlBEA, 0.36Zn-DeAlBEA, and 0.60Zn-DeAlBEA at ambient temperature in He. EXAFS spectra of ZnO, ZnCl₂, and Zn metal standards at ambient temperature in air are also shown. The spectra are offset for clarity. (C) Real and (D) imaginary components of the Fourier-transformed k^2 -weighted EXAFS of 0.12Zn-DeAlBEA at ambient temperature in He, and at 773 K in He. Solid lines show the measured spectra, and dashed lines show the fits to the data. The spectra are offset for clarity.

Table 1. Fitted Parameters for Fourier-Transformed Zn K-edge EXAFS of 0.12Zn-DeAlBEA acquired at Ambient Temperature and 773 K in He and Zn K-edge EXAFS of 0.36Zn-DeAlBEA reported in Ref. ⁶². Reproduced with permission from reference 62, Copyright 2021, American Chemical Society.

Sample Conditions	N	R [Å]	σ^2 [$10^{-3} \cdot \text{Å}$]
0.12Zn-DeAlBEA, Ambient temperature, He ^a	4.2 ± 0.9 (Zn-O)	1.95 ± 0.01	8.4 ± 2.5
0.12Zn-DeAlBEA, 773 K, He ^a	3.1 ± 0.6 (Zn-O)	1.87 ± 0.01	15.7 ± 2.4
	2.0 ± 1.0 (Zn-O)	1.88 ± 0.08	9 ± 5
0.36Zn-DeAlBEA, 773 K, He	0.8 ± 0.6 (Zn-(O)-Si)	3.12 ± 0.11	5 ± 5
	0.8 ± 0.8 (Zn-Zn)	2.66 ± 0.10	7 ± 2

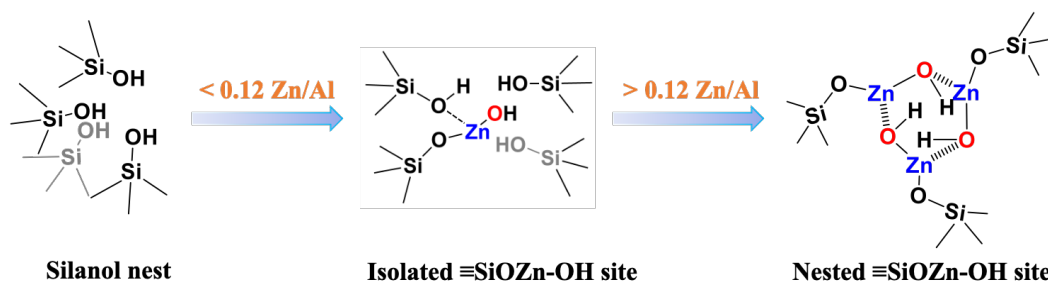
^aR-factor: 0.007. The amplitude reduction factor S_0^2 is 0.83 ± 0.14 . The inner potential correction ΔE_0 is 0.9 ± 0.8 .

Zn K-edge X-ray absorption spectroscopy (XAS) was used to further characterize the oxidation state and local coordination environment of Zn sites in Zn-DeAlBEA. XANES spectra of Zn-DeAlBEA taken at ambient temperature in He are shown in Figure 3A together with XANES spectra of metallic Zn, ZnO, and ZnCl₂. The corresponding Zn K-edge energies of Zn-DeAlBEA and of metallic Zn are calculated as the zero-crossing of the second derivative of the unnormalized absorption peak, are given in Table S2. The Zn-DeAlBEA samples all exhibit similar Zn K-edge energies that are comparable to those of standards containing Zn in the 2+ oxidation state. This conclusion is consistent with that drawn from XPS spectra. The XANES spectrum of 0.12Zn-DeAlBEA taken at 773 K in He is shown in Figure 3B. The Zn K-edge energy (see Table S2) in this case is slightly lower than that measured at room temperature, but remains in the range of energies characteristic of Zn²⁺ cations.

The real and imaginary Fourier components of the k^2 -weighted EXAFS (FT-EXAFS) spectra of Zn-DeAlBEA samples taken in He at 295 K are shown in Figure 4A-B, and those of 0.12Zn-DeAlBEA taken at 773 K in He are shown in Figure 4C-D. The real part of the FT-EXAFS patterns for Zn-DeAlBEA exhibit a peak at ca. 1.5 Å attributable to O backscattering in the first coordination shell of Zn²⁺ based on a comparison of the

imaginary component of the FT-EXAFS spectra of Zn-DeAlBEA to that of ZnO. In contrast to the FT-EXAFS patterns for metallic Zn and ZnO, the real part of the FT-EXAFS spectra of Zn-DeAlBEA do not exhibit features attributable to Zn backscattering in the first or second coordination shell of Zn^{2+} cations. This observation suggests that the Zn sites in Zn-DeAlBEA are isolated at room temperature. Similarly, the FT-EXAFS spectrum of 0.12Zn-DeAlBEA acquired at 773 K in He only shows evidence for Zn^{2+} cations coordinated to O atoms and the absence of Zn atoms in the nearest-neighbor or next-nearest neighbor positions.

The FT-EXAFS spectra of 0.12Zn-DeAlBEA were analyzed to determine the number of O atoms in the first coordination shell of Zn^{2+} cations both at 295 K and 773 K in He. The results are shown in Figure 4C-D and Table 1. At ambient temperature, Zn^{2+} cations are coordinated to 4 O atoms at an interatomic distance of 1.95 Å. Upon heating to 773 K in He, the Zn-O coordination number decreases to 3, due possibly to the removal of O atoms as water. A similar reduction in Zn-O coordination number has been proposed for Zn/SiO₂, heated initially in He at 723 K in He and then during propane dehydrogenation at 823 K.²² Table 1 also gives the coordination numbers and bond distances for a sample of Zn-DeAlBEA prepared with Zn/Al = 0.36, for which $\text{CN}_{\text{Zn-O}} = 2$, $\text{CN}_{\text{Zn-Zn}} = 1$, and $\text{CN}_{\text{Zn-O-Si}} = 1$. This information suggests weak interaction is present between neighboring Zn sites, which is consistent with the IR results of adsorbed pyridine and DTBPy and UV-vis results.



Scheme 1. Creation of isolated Zn open site and nested Zn-OH site in silanol nest of dealuminated BEA zeolite.

To summarize, dealumination of H-BEA removes all Al atoms and creates silanol

nests of four $\equiv\text{Si-OH}$ groups, in which OH species are H-bonded. After grafting Zn onto DeAlBEA zeolite, characterization of Zn sites in Zn-DeAlBEA by IR spectroscopy of adsorbed pyridine and DTBPy, UV-vis, XPS and XAS suggests that isolated $\equiv\text{SiOZn-OH}$ sites are formed at low Zn/Al ratios (< 0.12) and that above this ratio, nests of weakly interacting $\equiv\text{SiOZn-OH}$ sites are produced, as illustrated in Scheme 1. It is noted that both dimers and trimers of $\equiv\text{SiOZn-OH}$ groups are consistent with the characterization results of nested sites. As discussed below, these weak interactions between neighboring $\equiv\text{SiOZn-OH}$ sites enhance the catalytic activity of Zn for propane and n-butane dehydrogenation.

Propane dehydrogenation over Zn-DeAlBEA

The reaction of propane over Zn-DeAlBEA produces equimolecular amounts of propene and H_2 , and only small amounts of methane and ethene. Figure 5A presents the rates of propane conversion with time on stream (TOS) in 2 kPa of propane in He at 773 K over 0.12Zn-DeAlBEA and 0.36Zn-DeAlBEA. For both catalysts, the propane conversions were under differential conditions, $< 2.5\%$. For this propane feed concentration and reaction temperature the approach to equilibrium conversion (63.8%) is about 4.0%. Each catalyst exhibits a dehydrogenation selectivity of 94-96%. The effect of Zn/Al ratio on the rate of propane dehydrogenation is presented in Figure 5B. For the reaction conditions used, the conversion of propane is below 3.0% and the approach to equilibrium is below 5%. Consequently, the reaction rate measured experimentally can be regarded as the turnover frequency (TOF) for propane dehydrogenation. As shown in Figure 5B, the dehydrogenation TOF was observed to be constant for $\text{Zn/Al} < 0.12$, indicating the existence of isolated Zn atoms. As the Zn/Al ratio increases further from 0.12 to 0.36, the dehydrogenation rate increases almost linearly with Zn content, and then remains almost constant when the Zn/Al ratio is further increased to 0.60. While, for Zn-DeAlBEA with Zn/Al ratio of 1.0, a significant decrease in dehydrogenation activity is observed. These results suggest that propane dehydrogenation increases once nests of $\equiv\text{SiOZn-OH}$ species are formed (see Scheme

1) but decreases at high Zn/Al ratios when ZnO_x species begin to form.

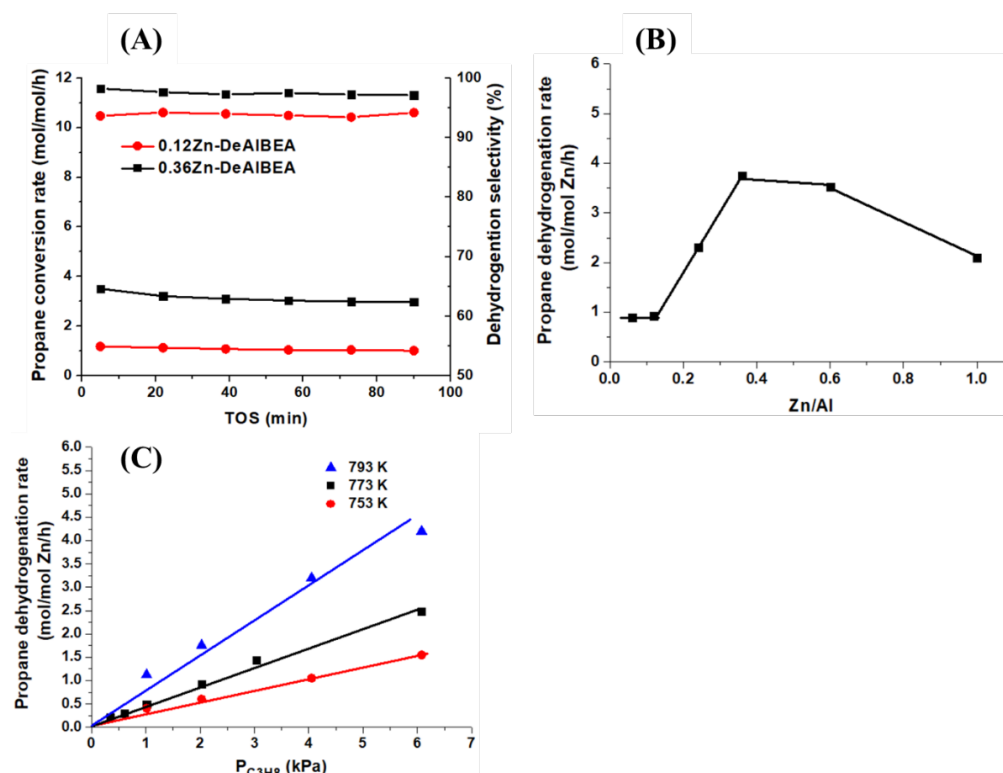
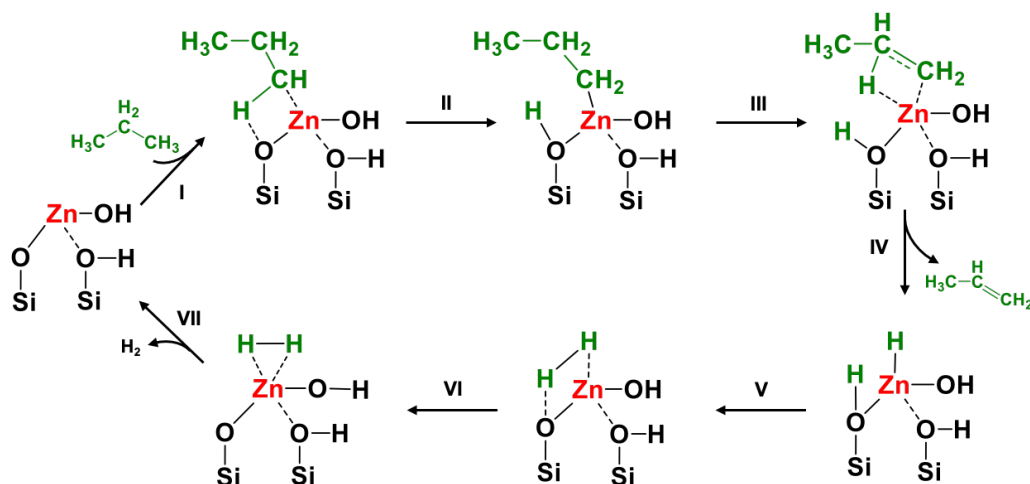


Figure 5. (A) Propane consumption rates and carbon selectivity to propene for 0.12Zn-DeAlBEA and 0.36Zn-DeAlBEA as a function of TOS, measured at 773 K with 2 kPa Propane/He. (B) Dependence of dehydrogenation rates on Zn/Al ratio measured at 773 K with 2 kPa Propane/He. Catalyst mass = 50 mg, total flow rate = 100 mL min⁻¹, TOS = 5 min. (C) Dependence of dehydrogenation rates for 0.12Zn-DeAlBEA with propane partial pressure measured at 773 K. Catalyst mass = 50 mg, total flow rate = 100 mL min⁻¹. Solid lines shown in Figure 5C are regressed fits of eqn. 1.

The dependence of rate of propane dehydrogenation on the propane partial pressure was investigated on 0.12Zn-DeAlBEA under differential conditions. The conversion of propane is <1.5% at the lowest propane partial pressure and the highest temperature employed. Under these conditions, the concentration of propene and H₂ are insignificant compared with that of reactant propane and hence the hydrogenation of propene back to propane is very low. As shown in Figure 5C and Figure S4, the measured dehydrogenation rate over 0.12Zn-DeAlBEA increases linearly with propane partial pressure up to about 20 kPa for temperature between 753 K and 793 K, indicating weak adsorption of propane on the isolated $\equiv\text{SiOZn-OH}$ sites contained in this catalyst. A similar linear increase in the rate of propane dehydrogenation with propane partial

pressure was also observed for 0.36Zn-DeAlBEA, below 6 kPa, but the rate of dehydrogenation decreases progressively with further increase in propane partial pressure, suggesting that the adsorption of propane is stronger on nested $\equiv\text{SiOZn-OH}$ sites observed for 0.36Zn-DeAlBEA compared to the isolated sites observed for 0.12Zn-DeAlBEA.

A possible mechanism for propane dehydrogenation on isolated $\equiv\text{SiOZn-OH}$ sites is proposed in Scheme 2 that is based on previously reported studies.^{4, 22} For simplification, the H-bonding interaction between Zn-OH and Si-OH groups contributed by local environment of zeolite is not illustrated in the steps that not directly correlate with this interaction. Propane first adsorbs onto the isolated Zn sites, with the methyl carbon interacting with the Lewis acid Zn and α -H interacting with the oxygen (O) of Si-O-Zn group. Then, direct α -hydride abstraction from the methyl group is proposed to occur, leading to a propyl group bonded to the Zn atom and an H atom bonded to the O atom of Si-O-Zn group. Subsequently, β -hydride elimination from the propyl groups over Zn-O-Si structure produces propene, which is expected to be the rate-limiting step as proposed by theoretical studies of propane dehydrogenation over isolated Zn and Ga site.^{4, 22} When nests of $\equiv\text{SiOZn-OH}$ sites are formed, as in the case of 0.36Zn-DeAlBEA, charge transfer between neighboring Zn-OH groups causes the nested Zn atom to become more Lewis acidic and the O atom in Si-O-Zn groups to become more Lewis basic, thereby facilitating the adsorption of propane and the heterolytic cleavage of β C-H bond. Following the formation of propene, desorption of propene and H_2 helps complete catalytic cycle and restore the active site.



Scheme 2. Proposed reaction mechanism for propane dehydrogenation over isolated $\equiv\text{SiOZn-OH}$ site.

Based on the dependence of the rates of propane dehydrogenation with propane partial pressure and the elementary steps outlined in Scheme 2a, the rate expression for propane dehydrogenation over isolated Zn sites is given by eqn. 1 (see the SI for a detailed derivation):

$$r_{C_3^-} = k_{C_3^-} K_{dis} K_{C_3^-} P_{C_3^-} \quad (1)$$

In eqn. 1, the parameter $k_{C_3^-}$ is the rate coefficient for β -hydride elimination of propane, while $K_{C_3^-}$ and K_{dis} are the equilibrium constants for propane physisorption (Scheme 2a, step I) and dissociative adsorption (Scheme 2a, step II) onto isolated Zn site, respectively. $P_{C_3^-}$ stands for the partial pressure of propane. According to the theoretical studies for propane dehydrogenation over single-site Zn^{2+} on silica²², $[\text{GaH}]^{2+}$ grafted over ZSM-5⁴ and single-site ZnOx/S-1 ⁴¹, eqn.1 was derived based on the assumptions that the adsorption and desorption of propane is quasi-equilibrated, the first C-H cleavage of methyl group is proposed to have low activation barrier and the rate-limiting step is the β -hydride elimination. Nonlinear least-squares regression of eqn. 1 with respect to the measured rates data shown in Figure 5C was conducted and the apparent first-order rate coefficients ($k_{C_3^-} K_{C_3^-} K_{dis}$) at all three temperatures are summarized in Table S3. The apparent activation energy for propane dehydrogenation

over 0.12Zn-DeAlBEA is 141 kJ/mol. The kinetics of propane dehydrogenation was also investigated for 0.36Zn-DeAlBEA between 753-793 K and propane partial pressures < 6 kPa. As seen in Figures S6A, the dehydrogenation rate is nearly first order in propane partial pressure. The apparent activation energy for propane dehydrogenation determined from an Arrhenius plot (see Figure S6) is 108 kJ/mol for 0.36Zn-DeAlBEA.

n-Butane dehydrogenation over Zn-DeAlBEA

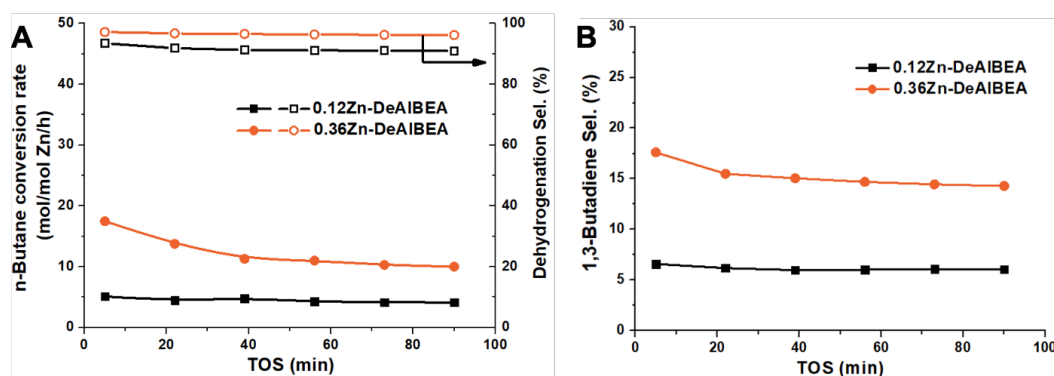


Figure 6. (A) n-Butane consumption rates and overall carbon selectivity to dehydrogenation products and (B) selectivity to 1,3-butadiene (1,3-BD) over 0.12Zn-DeAlBEA and 0.36Zn-DeAlBEA, measured at 773 K and 2.53 kPa n-butane/He, as a function of TOS. Solid symbols in Figure 6A are n-butane consumption rate, while open symbols are the overall selectivity to butenes and 1,3-BD.

The dehydrogenation of n-butane was investigated on 0.12Zn-DeAlBEA and 0.36Zn-DeAlBEA under conditions of differential conversion n-butane conversion (< 3%). Figure 6A shows that the initial rate of n-butane conversion normalized per Zn over 0.36Zn-DeAlBEA is about 3.3 times higher than that over 0.12Zn-DeAlBEA, suggesting that nests of $\equiv\text{SiOZn-OH}$ sites are more active than isolated $\equiv\text{SiOZn-OH}$ sites for n-butane dehydrogenation, consistent with what was observed for propane dehydrogenation. Both representative catalysts exhibit good selectivity to n-butane dehydrogenation compared with the C-C cracking, as evidenced by the high selectivity to total C₄ dehydrogenation products (ca. 97% for 0.36Zn-DeAlBEA and 92% for 0.12Zn-DeAlBEA). Detailed analysis of the dehydrogenation products for both catalysts are presented in Figure S7, which shows that trans-2-butene, 1-butene and cis-

2-butene are the main butene isomers, accompanied by only small amounts of isobutene (selectivity < 2.5%). Among the butene isomers, thermodynamically stable trans-2-butene and cis-2-butene account for overall selectivities of ca. 58% and 54.7% for 0.12Zn-DeAlBEA and 0.36Zn-DeAlBEA, respectively. It is also noted that 1,3-BD was produced with 6.6% selectivity over isolated $\equiv\text{SiOZn-OH}$ sites in 0.12Zn-DeAlBEA, and increased to 17.6% over nests of $\equiv\text{SiOZn-OH}$ sites in 0.36Zn-DeAlBEA. This high selectivity to 1,3-BD is significantly greater than that previously reported for non-noble catalyst and even some Pt-based catalyst.^{8, 63-65} For example, for n-butane dehydrogenation over Ni-Sn/SiO₂ the reported selectivity to 1,3-BD is only 3.4% at an n-butane conversion of 16.2% and 856 K.

The influence of space time on n-butane conversion over 0.12Zn-DeAlBEA, shown in Figures 7A-B, reveals that the selectivity to 1,3-BD increases with increasing space time and is accompanied by a decrease in the selectivity to trans-2-butene, cis-2-butene and 1-butene, indicating that 1,3-BD is generated via secondary dehydrogenation of linear butene isomers. Similar behavior is observed over nest of $\equiv\text{SiOZn-OH}$ sites in 0.36Zn-DeAlBEA (Figure S8).

The effect of reaction temperature on n-butane dehydrogenation for 0.12Zn-DeAlBEA is also investigated. For the reaction conditions used, n-butane conversion was < 1% and the approach to equilibrium was negligible. As shown in Figure S9A, the rate of n-butane dehydrogenation increases from approximately 4 mol/mol Zn/h at 773 K to 7.3 mol/mol Zn/h and 13.5 mol/mol Zn/h at 793 and 823 K, respectively and Figure S9B shows that the selectivity to 1,3-BD also increases with increasing temperature.

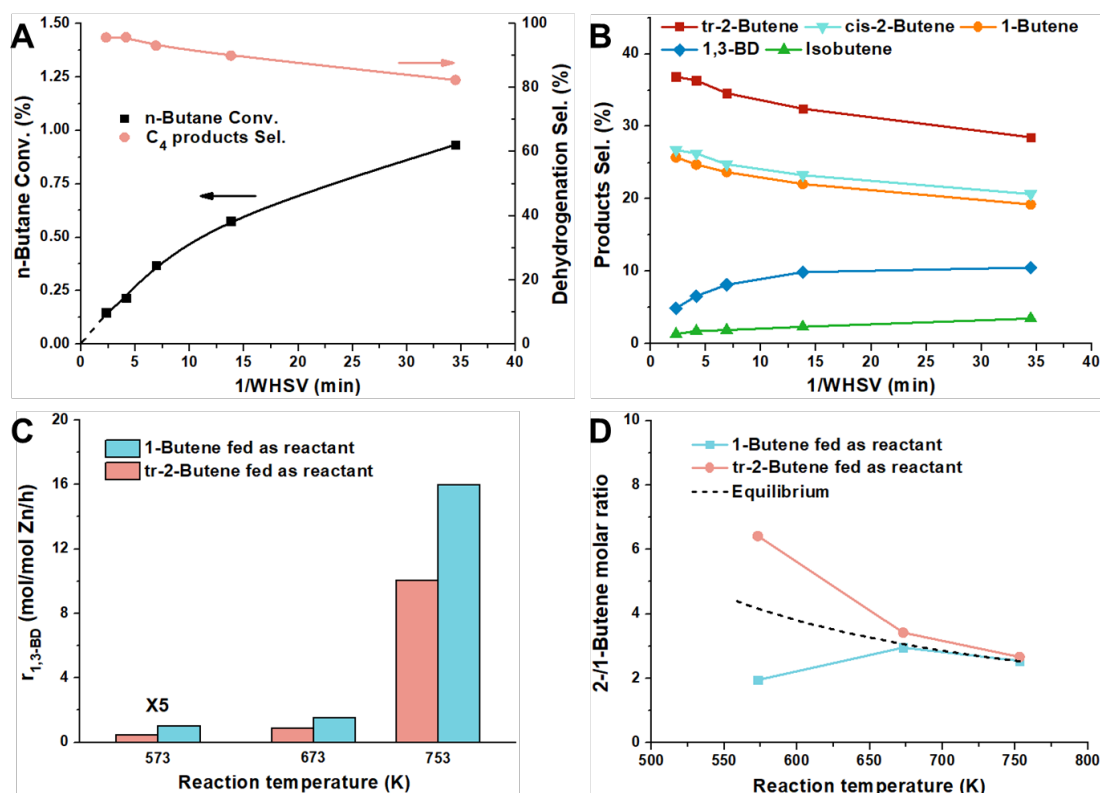


Figure 7. Effects of space time on (A) the consumption of n-butane and overall carbon selectivity to C₄ dehydrogenation products, and (B) the detailed products selectivity to each component of C₄ products during n-butane reaction over 0.12Zn-DeAlBEA, measured at 753 K with 2.53 kPa n-butane/He. The dashed line in Figure 7A is guide for the eye. (C) Rates of 1,3-BD formation from 1-butene and trans-2-butene dehydrogenation over 0.36Zn-DeAlBEA as a function of temperature. The rates of 1,3-BD formation at 573 K are magnified 5 times for clarify. (D) Molar ratios of 2-butene to 1-butene for 1-butene and trans-2-butene conversion over 0.36Zn-DeAlBEA as a function of temperature. The dashed line shown in Figure 7D is the 2-butene/1-butene molar ratios at equilibrium for each temperature.

To clarify the reaction pathways for the conversion of n-butane to 1,3-BD, the rate of 1,3-BD formation from 1-butene and trans-2-butene was investigated. Since transformation between 1-butene and 2-butene is unavoidable and butene can then undergoes dehydrogenation to produce 1,3-BD, both butene isomers can be regarded as unconverted feedstock. Therefore, the conversion of 1-butene or trans-2-buten are calculated to be 2.6% and 2.4%, respectively, at the highest tested temperature of 753 K. We note that under this feed condition, the conversion of butene isomers is far from the equilibrium and hence the reversible hydrogenation of butene to butane can be

neglected. As shown in Figure 7C, the rate of 1,3-BD formation from 1-butene is always more rapid than from trans-2-butene. Specifically, the ratio of 1,3-BD formation rate from 1-butene to trans-2-butene increases from 1.5 to 1.7 and then to 2.2 as the temperature decreases from 753 to 673 and then to 573 K. This result indicates that 1,3-BD is formed primarily via the dehydrogenation of 1-butene. The generation of 1,3-BD from trans-2-butene more likely proceeds via isomerization of this isomer to 1-butene, consistent with the observed rapid isomerization of 1-butene to trans-2-butene. As shown in Figure 7D, this process occurs more rapidly at higher temperature and reaches an equilibrium ratio above 673 K.

Figure 8 shows the rate of n-butane dehydrogenation over Zn-DeAlBEA with different Zn/Al ratios, at 773 K for a feed containing 2.53 kPa n-butane in He. The rate of n-butane dehydrogenation increases with Zn content up to a Zn/Al = 0.6, beyond which the rate decreases. It is noted that DeAlBEA is not active for n-butane dehydrogenation. Figure 8B shows the rate of n-butane dehydrogenation normalized per moles of Zn (TOF). The TOF for n-butane dehydrogenation is approximately independent of Zn content with Zn/Al ratio up to 0.12 and then increases monotonically with Zn/Al up to a ratio of 0.36, after which an almost constant activity is obtained as the Zn/Al ratio increases to 0.60. These observations are similar to those reported above for propane dehydrogenation.

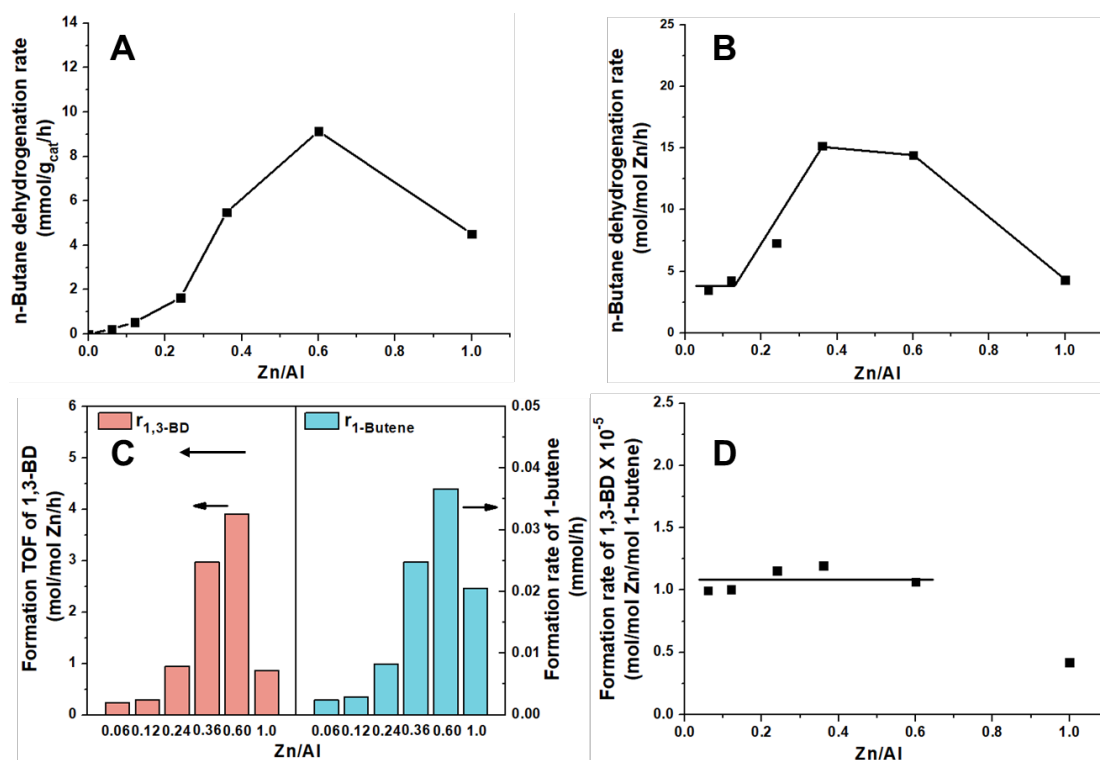


Figure 8. Rates of n-butane dehydrogenation (rates of total butenes and 1,3-BD formation), measured at 2.53 kPa n-butane/He and 773 K, as a function of Zn/Al ratio. (A) Rates normalized per catalyst mass. (B) Rates normalized per moles of Zn. (C) Rates of 1,3-BD formation and 1-butene formation normalized per moles of Zn in both cases. (D) Rates of 1,3-BD formation normalized per moles of Zn and 1-butene. Solid lines in Figures 8A, B and D are guide for the eye.

Figure 8C shows the rate of 1,3-BD formation from n-butane normalized per Zn atom measured at differential conversion (n-butane conversion < 4.5%), as a function of the Zn/Al ratio. The TOF for 1,3-BD formation is independent of Zn content for $\text{Zn/Al} < 0.12$, and then increases monotonically as the Zn/Al ratio increases to 0.6, beyond which it decreases significantly. As found for the effects of space-time discussed above, 1-butene is the precursor to 1,3-BD. Interestingly, the rate of 1-butene formation exhibits a trend with increasing Zn/Al ratio similar to that for the TOF for 1,3-BD formation. This observation suggests that the rate of 1,3-BD (a secondary product) formation is proportional to the concentration of 1-butene (the primary product). Consistent with this idea, the rate of 1,3-BD formation normalized by the rate of 1-butene formation, is nearly independent of the Zn/Al ratio below 0.6 under current conditions (see Figure 8D). This interesting finding indicates that despite the generation

of nested $\equiv\text{SiOZn-OH}$ sites and their enhanced activity of alkane dehydrogenation, each grafted Zn atoms is equally active for secondary dehydrogenation of 1-butene to 1,3-BD.

To further confirm the effects of Zn content on 1-butene dehydrogenation to 1,3-BD, 1-butene was fed directly as a reactant over catalysts with Zn/Al ratios of 0.12, 0.36, and 0.60. The results of these experiments are presented in Figure S10. As expected, under identical reaction condition, the observed 1,3-BD TOF for 1-butene is approximately independent of the Zn content up to a Zn/Al ratio of 0.60 for TOSs < 90 min, suggesting that the activity of Zn atoms for 1-butene dehydrogenation on either isolated or nested $\equiv\text{SiOZn-OH}$ sites is identical. This is consistent with the independence of the rate of 1,3-BD formation normalized by per mole of Zn and per mole of 1-butene with Zn loading shown in Figure 8D.

Kinetics of n-butane and 1-butene dehydrogenation over Zn-DeAlBEA

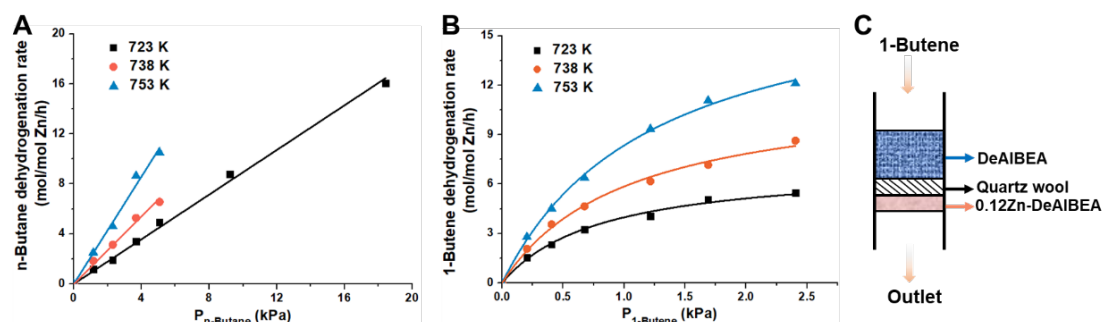


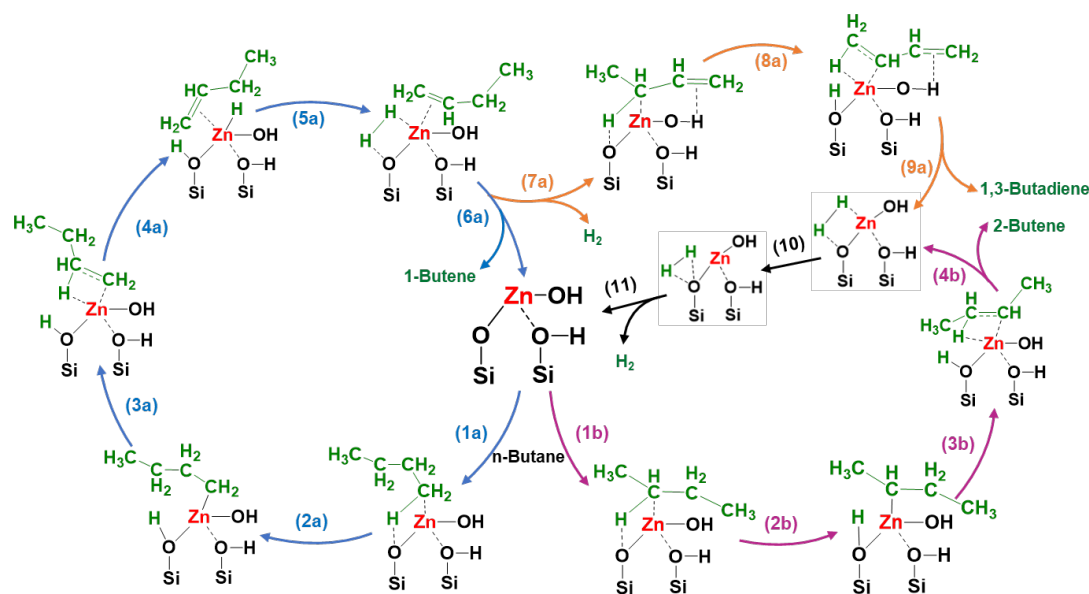
Figure 9. (A) Dependence of the rates of n-butane dehydrogenation on the n-butane partial pressure, measured at 723 K, 738 K and 753 K over 0.12Zn-DeAlBEA. Solid lines shown in Figure 9A are regressed fits of eqn. 2 to the data. (B) Dependence of the rate of 1-butene dehydrogenation on the 1-butene partial pressure, measured at 723 K, 738 K and 753 K over the 0.12Zn-DeAlBEA. Solid lines shown in Figure 9B are regressed fits of eqn. 3 to the data. (C) Schematic illustration of the catalyst bed for the kinetic studies of 1-butene dehydrogenation. 40 mg of 0.12Zn-DeAlBEA is placed below 150 mg of DeAlBEA, separated by an inert layer of quartz wool. DeAlBEA is used to equilibrate the isomerization of 1-butene to 2-butene (no dehydrogenation activity is detected in this process).

The kinetics of n-butane and 1-butene dehydrogenation were measured separately

in order to obtain a better understanding of the consecutive dehydrogenation steps. The first dehydrogenation step, n-butane dehydrogenation to butenes, was investigated over 0.12Zn-DeAlBEA. Figure 9A shows the rate of butene isomer formation as functions of temperature and n-butane partial pressure measured under differential reaction conditions (n-butane conversion < 1%). It should be noted that in these experiments only n-butane dehydrogenation occurs and the formation of 1,3-BD is negligible. At 723 K, n-butane dehydrogenation increases linearly with n-butane partial pressure up to 18.4 kPa, indicating the weak interaction between n-butane and isolated Zn sites, similar to what was observed for propane dehydrogenation. At the other two temperatures of 738 and 753 K, first order dependence for the rate of n-butane dehydrogenation on n-butane partial pressure was obtained experimentally up to a partial pressure of 5.5 kPa. Considering that adsorption of n-butane becomes weaker at higher temperature, a linear dependence on partial pressure is expected up to higher n-butane partial pressure for reaction carried out at 738 and 753 K. However, over 0.36Zn-DeAlBEA (Figure S11A), the rate of n-butane dehydrogenation increases linearly with n-butane partial pressures for low partial pressures < 4 kPa but then increases less rapidly at higher pressures, indicating the stronger adsorption of n-butane over nest of $\equiv\text{SiOZn-OH}$ sites compared with isolated $\equiv\text{SiOZn-OH}$ sites. The kinetics of n-butane dehydrogenation over nested $\equiv\text{SiOZn-OH}$ sites in 0.36Zn-DeAlBEA were conducted for n-butane conversion < 2%, using an n-butane partial pressure of 2.3 kPa and temperatures of 708 K to 753 K. The Arrhenius plot for n-butane conversion is shown in Figure S11B. As evaluated, the apparent activation energy of n-butane dehydrogenation over $\equiv\text{SiOZn-OH}$ nests is 82 kJ/mol.

Since isolated $\equiv\text{SiOZn-OH}$ sites and nest of such sites exhibit similar TOFs for 1-butene dehydrogenation, the kinetics of 1-butene dehydrogenation to 1,3-BD was determined using 0.12Zn-DeAlBEA. It should be noted that rapid isomerization of 1-butene to thermodynamically more stable 2-butene always accompanies this process, as shown in Figure 7D. To mitigate the influence of isomerization on the kinetics of 1-butene dehydrogenation, thermodynamic equilibration of butene isomers should be

established prior to the dehydrogenation of 1-butene to 1,3-BD. To this end, it was found that H-bonded silanol nests in DeAlBEA, which have weak Lewis acidity, can catalyze the isomerization of 1-butene⁶⁶ (Figure S12A), with almost no dehydrogenation (the yield of 1,3-BD is < 0.05% at 1/WHSV = 15 min, the space time is calculated via dividing the mass of DeAlBEA by mass flow rate of 1-butene (Figure S12B)). Equilibrated isomerization of 1-butene was easily established for mass-based space times greater than 15 min. Therefore, a catalyst bed in which DeAlBEA is placed on top of 0.12Zn-DeAlBEA was used to study the kinetics of 1-butene dehydrogenation (see Figure 9C). Under these conditions, quasi-equilibrated isomerization of 1-butene to 2-butene was achieved prior to dehydrogenation of 1-butene, as evidenced by the 2-/1-butene molar ratio, which is identical to that at thermodynamic equilibrium (Figure S12D). Moreover, the yield of 1,3-BD increases almost linearly as the space time relevant to 0.12Zn-DeAlBEA increases to about 5 min as shown in Figure S12C. Figure 9B shows the rates of 1-butene dehydrogenation as functions of 1-butene partial pressure and temperature. As demonstrated, the rates of 1-butene dehydrogenation increases linearly with 1-butene partial pressure at low partial pressures and then increases further but at a lower rate for higher 1-butene partial pressures for the three temperatures explored. Compared with the linear dependence of n-butane dehydrogenation on n-butane partial pressure, the observed partial pressure dependence on 1-butene suggests that the adsorption of 1-butene is much stronger than that of n-butane over the isolated $\equiv\text{SiOZn-OH}$ sites. It is noted that for all three temperatures examined (Figure S13), the molar ratios of 2-/1-butene is independent of 1-butene partial pressure, which is close to the value expected for thermodynamic equilibrium at each temperature. This finding supports the assumption that equilibrium isomerization of 1-butene/2-butene isomers is achieved before butene dehydrogenation occurs.



Scheme 3. Proposed reaction mechanism for n-butane dehydrogenation over isolated Zn sites.

Scheme 3 illustrates our proposed mechanism for n-butane dehydrogenation to butene isomers and the subsequent dehydrogenation of 1-butene to 1,3-BD. The H-bonding interaction between Zn-OH and Si-OH groups is not present for simplification. This possible mechanism is analogous to the alkyl-mediated mechanism proposed for n-butane dehydrogenation over Ga-ion exchanged MFI and $\text{Cr}_2\text{O}_3(0001)$.^{67, 68} The first step is physisorption of n-butane molecules over $\equiv\text{SiOZn-OH}$ sites via methyl group (step 1a) or methylene group (step 1b). This step is proposed to be followed by the formation of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{-Zn}$ and $\text{CH}_3\text{CH}_2(\text{CH}_3)\text{CH-Zn}$ species via either methyl C-H cleavage (step 2a) or methylene C-H cleavage (step 2b) of physisorbed n-butane. The next step is rate-limiting β -hydride elimination from the alkyl fragment to produce 1-butene and H_2 (steps 3-6a) or 2-butene and H_2 (steps 3-4b, 10-11). Formation of 1-butene is slightly more probable as the activation barrier for this step is slightly lower for hydrogen removal from the terminal methyl carbon, in agreement with the experimental result that 1-butene is produced as primary product from n-butane dehydrogenation. Some of the generated 1-butene is expected to undergo further heterolytic C-H cleavage at the methylene group and subsequent β -hydride elimination

to produce 1,3-BD and H₂. to produce 1,3-BD and H₂. This process involves a transition state in which the C=C bond of 1-butene is stabilized by the proton of Zn-OH forming a π -complex intermediate, mirroring the adsorption of 1-butene on ZnO⁶⁹ and the H-form of zeolites⁷⁰. The DBTPy-adsorbed FTIR spectra characterizing the weak Brønsted acidity of H-bonded $\equiv\text{SiOZn-OH}$ and Si-OH sites consolidate this speculation. Desorption of H₂ (step 11) completes the reaction cycle.

From the investigation of the activities of propane, n-butane and 1-butene dehydrogenation over Zn sites, it is observed that nested $\equiv\text{SiOZn-OH}$ sites exhibit a superior dehydrogenation activity per Zn atom for propane dehydrogenation to propene and n-butane dehydrogenation to butenes, but no change in the specific activity for 1-butene dehydrogenation to 1,3-BD relative to Zn-DeAlBEA containing only isolated $\equiv\text{SiOZn-OH}$ sites. We note that the kinetics of propane and n-butane dehydrogenation are different compared to 1-butene dehydrogenation. For the alkane dehydrogenation, the rates of alkane dehydrogenation are first order in the propane and n-butane partial pressure up to a value of about 18.4 kPa, respectively, suggesting weak adsorption of both propane and n-butane over isolated Zn sites. Over nested Zn sites, a decrease in the reaction order with reactant partial pressure is observed at lower propane and n-butane partial pressure. This indicates that adsorption of propane and n-butane are stronger on nested Zn sites compared to the isolated ones. By contrast, in the case of 1-butene dehydrogenation over isolated $\equiv\text{SiOZn-OH}$ sites, the rate of 1,3-BD formation exhibits a Langmuir-Hinshelwood dependence on 1-butene partial pressure, suggesting an obviously strong adsorption of 1-butene over isolated Zn sites and it follows that even stronger adsorption of 1-butene is expected over nested Zn sites. Due to the strong adsorption of 1-butene, it is hypothesized that the weak interaction between neighboring $\equiv\text{SiOZn-OH}$ groups in nested Zn sites would be interrupted and the improvement in the rate-limiting β -hydride elimination step would be offset. Consequently, the difference in catalytic activity of isolated and nested $\equiv\text{SiOZn-OH}$ sites for alkane dehydrogenation and 1-butene dehydrogenation is most likely due to the strength of reactant adsorption over these two kinds of active sites. The elementary

steps shown in Scheme 3 were used to derive rate expressions for n-butane and 1-butene dehydrogenation, eqns. 2 and 3 (see the SI for detailed derivation):

$$r_{C_4^-} = k_{C_4^-} K_{C_4^-} K_{dis-B} P_{C_4^-} \quad (2)$$

$$r_{C_4^=} = \frac{k_{C_4^=} K_{C_4^=} K_{dis-1B} A P_{C_4^=}}{1 + K_{C_4^=} K_{dis-1B} A P_{C_4^=}} \quad (3)$$

These equations are derived on the assumptions that the adsorption of n-butane and 1-butene are quasi-equilibrated and that β -hydride elimination involved in n-butane and 1-butene dehydrogenation are rate limiting. Furthermore, since the kinetics of both n-butane and 1-butene dehydrogenation are conducted at differential conversions, the hydrogenation of butene to n-butane and 1,3-BD to butene should not be significant due to the low H_2 concentration in the reaction systems. Therefore, it is also assumed that both dehydrogenation reactions are irreversible. In eqns. 2 and 3, $k_{C_4^-}$ and $k_{C_4^=}$ are the rate coefficients for n-butane dehydrogenation and 1-butene dehydrogenation (steps 4a and 9a), respectively; $K_{C_4^-}$ and $K_{C_4^=}$ are the equilibrium constants for the adsorption of n-butane and 1-butene onto Zn sites, respectively; K_{dis-B} and K_{dis-1B} are the equilibrium constants for the dissociative adsorption of n-butane and 1-butene onto Zn sites, respectively; A is the molar ratio of 1-butene partial pressure following thermodynamic equilibration of 1- and 2-butene isomers with respect to the initial 1-butene partial pressure fed to the reactor at specific temperature; and $P_{C_4^-}$ and $P_{C_4^=}$ are the partial pressures of n-butane and 1-butene fed, respectively. Nonlinear least-squares regression of eqns. 2 and 3 with respect to the measured rates data shown in Figure 9 were conducted. An R^2 of 0.99 was obtained for fits of eqns. 2 and 3 to the experimentally measured rates of n-butane and 1-butene dehydrogenation, as shown in Figure S14. The apparent first-order rate coefficients ($k_{C_4^-} K_{C_4^-} K_{dis-B}$) for n-butane dehydrogenation as well as fitted rate coefficients ($k_{C_4^=}$) and adsorption equilibrium constants ($K_{C_4^=} K_{dis-1B}$) for 1-butene dehydrogenation to 1,3-BD are summarized in Tables S3-S6.

Apparent activation energy (E_{app}) for n-butane dehydrogenation over isolated $\equiv SiOZn-OH$ sites and nests of $\equiv SiOZn-OH$ sites were obtained from Arrhenius plots

and are listed in Table 2. For n-butane dehydrogenation over isolated $\equiv\text{SiOZn-OH}$ sites, the apparent activation energy is 132 kJ/mol, which is considerably higher than that for $\equiv\text{SiOZn-OH}$ nests (82 kJ/mol). This is the same trend was noted above for propane dehydrogenation. While attempts were made to measure the apparent activation energy for 1-butene dehydrogenation over $\equiv\text{SiOZn-OH}$ nests, this could not be done due to deactivation of the catalyst in this case.

Also shown in Table 2 are the intrinsic activation barrier for 1-butene dehydrogenation (E_a) and the adsorption enthalpy of 1-butene ($\Delta H_{dis-ads}^*$) estimated from the Arrhenius and van't Hoff plots shown in Figure S16. The experimentally determined intrinsic activation barrier is 143.6 kJ/mol, whereas the adsorption enthalpy for 1-butene is -71.6 kJ/mol, leading to an apparent activation energy of 72 kJ/mol. As reported previously, the adsorption enthalpy of butane on metal oxides is typically in the range of -34 – -51 kJ/mol, and is about -39 kJ/mol on the surface of ZnO.⁷¹ If this value is taken as the n-butane adsorption enthalpy on the nested $\equiv\text{SiOZn-OH}$ sites, the intrinsic activation barrier for C-H cleavage of n-butane is estimated to be ~ 120 kJ/mol, which is slightly lower than that for C-H bond cleavage in 1-butene, this relationship is consistent with what we observed for kinetics study of n-butane dehydrogenation over 0.04Pt-0.36Zn-DeAlBEA and 0.02Pt-2.4Zn-SPP.^{62, 72, 73} The value of the intrinsic activation barrier for C-H cleavage in n-butane and 1-butene are both higher than those reported for 0.04Pt-0.36Zn-DeAlBEA (80.8 and 90.3 kJ/mol) and 0.02Pt-2.4Zn-SPP (60.7 and 75.3 kJ/mol). However, the value for n-butane dehydrogenation in this work is close to that reported for $\text{Cr}_2\text{O}_3(0001)$ (134 kJ/mol), Pt/Mg(Al)(In)O (129.4 kJ/mol) and PtSn/ Al_2O_3 (117.2 kJ/mol).^{68, 72}

Table 2. Experimentally measured activation energies for n-butane and 1-butene dehydrogenation over isolated and nested $\equiv\text{SiOZn-OH}$ sites.

All energies (kJ/mol)	n-butane dehydrogenation	1-butene dehydrogenation		
	E_{app}^a	$\Delta H_{dis-ads}^*$	E_a^b	E_{app}^a
isolated $\equiv\text{SiOZn-OH}$ sites	132	-72	144	72
nested $\equiv\text{SiOZn-OH}$ sites	82			

*Enthalpy for dissociative adsorption of 1-butene (associated with $K_{C_4}=K_{dis-1B}$);

dis-ads means dissociative adsorption;

^aApparent activation energy for n-butane and 1-butene dehydrogenation;

^bIntrinsic activation barrier for 1-butene dehydrogenation.

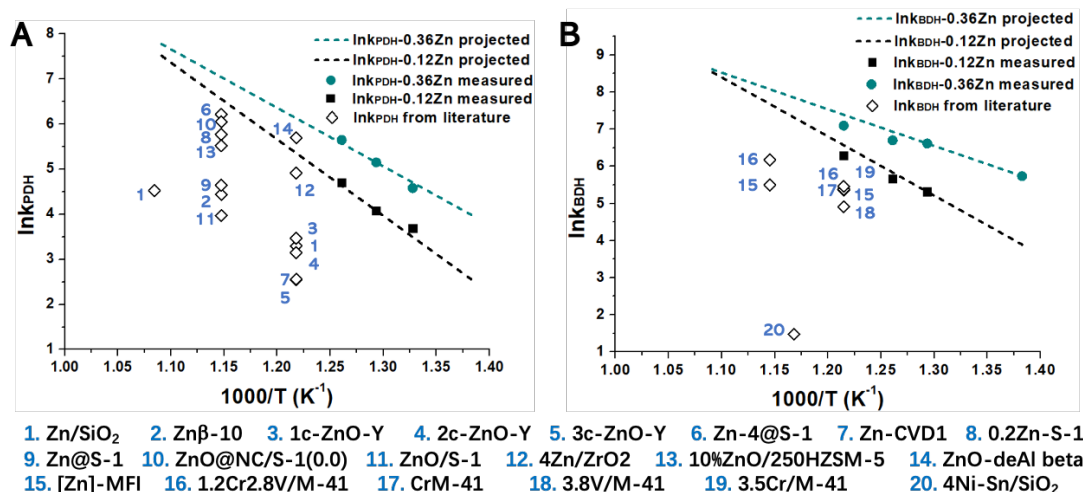


Figure 10. Comparison of the values of (A) k_{PDH} [mol propene (mol Zn sites·bar·h)⁻¹] and (B) k_{BDH} [mol butene (mol M sites·bar·h)⁻¹] for 0.12Zn-DeAlBEA and 0.36Zn-DeAlBEA with values reported previously for non-noble metal catalysts (open symbols) determined from the literature. Further details for each catalyst are given in Table S6. The black and blue dashed lines in panel (A) are projected based on the k_{PDH} values (solid symbols) at 773 K and the apparent activation energy of propane dehydrogenation for 0.12Zn-DeAlBEA and 0.36Zn-DeAlBEA, respectively. The black and blue dashed lines in panel (B) are projected based on the k_{BDH} values (solid symbols) at 773 K and the apparent activation energy of n-butane dehydrogenation for 0.12Zn-DeAlBEA and 0.36Zn-DeAlBEA, respectively.

Comparison of the activity of different catalysts for alkane dehydrogenation reported by different researchers is difficult because each research group uses different feed compositions (partial pressures), temperatures, and space times. Thus, to compare the activity of Zn-DeAlBEA with those reported previously for non-noble metal catalysts, effective forward rate coefficients for propane dehydrogenation (k_{PDH}) and n-butane dehydrogenation (k_{BDH}) were determined (see detailed information in SI, the detailed derivation for these two coefficients were reported in Ref. ^{62, 72}). Table S7 lists the most recently reported data for propane dehydrogenation over Zn-based catalysts, together with results for other non-noble metal catalysts such as Sn, Cr, and V. This

table also lists the elemental compositions of each catalyst and the reaction conditions used. Figure 10 compares the calculated values of k_{PDH} and k_{BDH} over isolated and nested $\equiv\text{SiOZn-OH}$ sites with other non-noble metal catalysts (mainly Zn-based catalysts) reported in the literature. The dashed lines indicate the effective forward rate constants for 0.12Zn-DeAlBEA and 0.36Zn-DeAlBEA at temperature between 723 and 923 K, which are projected using the calculated values at 773 K and the apparent activation energies for propane and n-butane dehydrogenation. To verify the projected values of k_{PDH} and k_{BDH} , values of the rate constants at other temperatures of 723, 753 and 793 K were compared with values of these parameters measured experimentally and are presented in Figure 10 as solid symbols. For both propane and n-butane dehydrogenation, the values are very close to the dashed lines, suggesting good consistency between the apparent activation energies estimated from the effective forward rate constants and those obtained by the kinetics investigation.

The result in Figure 10 shows that values of k_{PDH} and k_{BDH} for both isolated and nested $\equiv\text{SiOZn-OH}$ sites are higher than those for most non-noble metal-based catalysts previously reported. It should be noted, though, that propane dehydrogenation over ZnOx-S-1_1(H₂) exhibits the best activity among the catalysts reported with a value of k_{PDH} of 605 mol/mol Zn/h/bar at 873 K⁷⁴, which is higher than the value projected for 0.36Zn-DeAlBEA (493 mol/mol Zn/h/bar), at the same temperature. In the case of n-butane dehydrogenation, the Zn-DeAlBEA prepared in this study are superior to all other catalysts reported previously. The effective forward rate constants k_{BDH} on 0.12Zn-DeAlBEA and 0.36Zn-DeAlBEA are 3.2 and 7.3 times higher than that for 1.2Cr2.8V/M-41 (220.4 mol/mol M/h/bar) at 823 K.

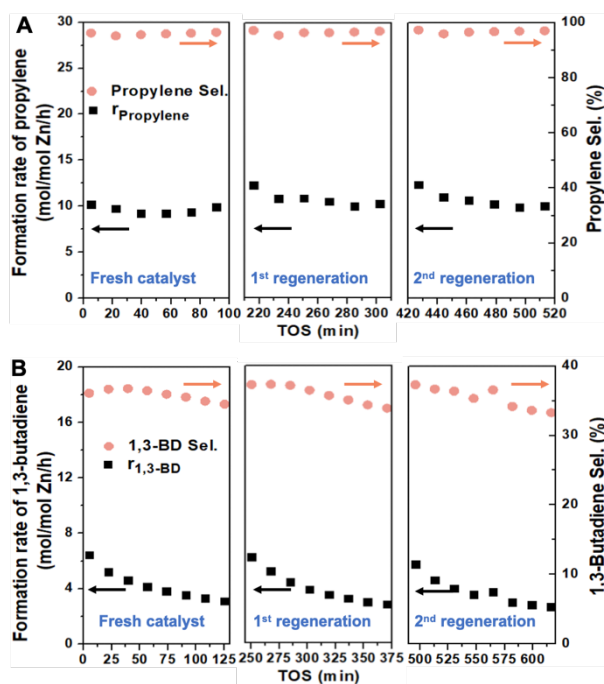


Figure 11. Illustrations of the regenerability of 0.60Zn-DeAlBEA for (A) propane dehydrogenation and (B) n-butane dehydrogenation. Reaction conditions: $m_{\text{cat}} = 50\text{mg}$ for PDH and 100 mg for BDH; dehydrogenation of propane is conducted at 823 K with 5.07 kPa propane/He; dehydrogenation of n-butane is conducted at 823 K with 2.53 kPa n-butane/He. Catalyst used is regenerated with a mixture of 20 mL/min He and 20 mL/min air at 823 K for 2 h.

0.6Zn-DeAlBE, which contains the highest concentration of nested $\equiv\text{SiOZn-OH}$ sites was tested for its stability and ability to be regenerated for propane dehydrogenation and n-butane dehydrogenation to 1,3-BD at 823K (Figure 11). For propane dehydrogenation, 0.6Zn-DeAlBEA exhibits an activity of 10 mol/(mol Zn·h) and 95% selectivity to propene. This activity is more than 10 times higher than that previously reported Zn/SiO₂.²² For n-butane dehydrogenation to 1,3-BD, 0.6Zn-DeAlBEA catalyst exhibits an activity of 6 mol/(mol Zn·h) for 1,3-BD formation activity and a selectivity to 1,3-BD of 35%. For both processes, 0.6Zn-DeAlBEA can be regenerated two times without a loss in activity, suggesting good stability of the nested Zn sites-loaded catalyst. Since the activity of isolated Zn sites is lower than that of nested $\equiv\text{SiOZn-OH}$ sites for alkane dehydrogenation, the loss of isolated $\equiv\text{SiOZn-OH}$ was not explored. The stability of Zn-DeAlBEA to loss of Zn under this reaction condition would be due to the possibility that nested $\equiv\text{SiOZn-OH}$ sites are resistant to

being reduced to metallic Zn and then volatile Zn hydrides and avoid the Zn sublimation. In addition to Zn loss by formation of zinc hydride, coke deposition also needs to be considered as a cause for catalyst deactivation. Thermogravimetric analysis (TGA) of spent 0.60Zn-DeAlBEA after both propane dehydrogenation and n-butane dehydrogenation was carried out and the TGA profiles of each are given in Figure S17. As shown, both spent catalysts exhibit two weight loss signals at around 393 K and 393~823K. The first loss is ascribed to sample dehydration and the second one is due to combustion of deposited coke deposit. The spent catalyst weight losses caused by coke combustion was 1.3% and 2.1%, respectively, for propane and n-butane dehydrogenation reactions.

Conclusions

Zn Lewis acid centers having an open site structure of $\equiv\text{SiOZn-OH}$ were grafted into the silanol nest created by dealumination of BEA zeolite and then investigated for both propane dehydrogenation to propene and n-butane dehydrogenation to 1,3-BD. Independent of Zn/Al ratio, Zn is found to be present as $\equiv\text{SiOZn-OH}$ sites. For Zn/Al ≤ 0.12 , these sites are isolated from each other, but as the Zn/Al ratio increases from 0.12 to 0.36, $\equiv\text{SiOZn-OH}$ nests are formed in which weak interaction between adjacent Zn centers and H-bonding interaction between Zn-OH and Si-OH groups occur, as shown in Scheme 1. In the investigation of the activity of propane and n-butane dehydrogenation, identical TOFs for Zn-DeAlBEA with Zn/Al ratios ≤ 0.12 are observed. As the Zn/Al ratio increases from 0.12 to 0.36, both reactions exhibit a linear increase of dehydrogenation TOFs for the formation of propene and butene isomers, demonstrating the advantage of $\equiv\text{SiOZn-OH}$ nest sites for light alkane dehydrogenation. The activity of Zn-DeAlBEA for 1-butene dehydrogenation to 1,3-BD is identical for Zn/Al ratios of 0.12 to 0.60. To elucidate the difference in catalytic activity, the mechanism and kinetics of propane, n-butane and 1-butene dehydrogenation reactions were investigated systematically over isolated and nested $\equiv\text{SiOZn-OH}$ sites. As revealed, weak interactions between Zn-OH groups of nested $\equiv\text{SiOZn-OH}$ sites

enhanced the adsorption of both alkanes on nested compared to isolated $\equiv\text{SiOZn-OH}$ sites. Furthermore, 1-butene adsorbs much stronger than propane and n-butane with $\equiv\text{SiOZn-OH}$ sites, which would interrupt such interaction among nested sites and the improvement in dehydrogenation activity would be offset. Rate expressions based on proposed mechanisms for the dehydrogenation of propane, n-butane and 1-butene were developed and were found to give very good representations of the experimentally observed rates. 0.6Zn-DeAlBEA was tested for its stability for propane and n-butane dehydrogenation reactions at 823K. For n-butane dehydrogenation to 1,3-BD, 0.6Zn-DeAlBEA exhibits a TOF of $\sim 6 \text{ mol}/(\text{mol Zn}\cdot\text{h})$ and a 1,3-BD selectivity of 35%, which are the best reported to date for non-noble metal-based catalysts. We also observed that 0.6Zn-DeAlBEA could be fully regenerated two times without losing any activity, suggesting a good stability of Zn atoms in nested $\equiv\text{SiOZn-OH}$ sites.

Associated content

Supporting Information

Experimental section including the catalyst synthesis, characterization techniques and catalyst evaluation; IR spectra of surface hydroxyl groups and IR spectra following pyridine adsorption of H-BEA and DeAlBEA (Figure S1); XRD, ICP, BET, UV-vis results of Zn-DeAlBEA (Figures S2, S3, Table S1); kinetics results for propane dehydrogenation (Figures S4, S5, S6), n-butane dehydrogenation (Figures S11, S15) and 1-butene dehydrogenation (Figure S16); supplemental reaction results for n-butane dehydrogenation (Figure S7); effects of space time, temperature and Zn loadings on n-butane dehydrogenation (Figures S8, S9, S10); effects of space time and temperature on the isomerization of 1-butene and trans-2-butene (Figures S12 and S13); parity plots for the dehydrogenation rates of n-butane and 1-butene obtained experimentally and fitted from kinetics equations (Figure S14); thermogravimetric profiles of spent catalyst; rate coefficients for propane dehydrogenation, n-butane dehydrogenation and 1-butene dehydrogenation obtained at different temperature (Tables S2, S3, S4, S5); summary of catalytic data for propane and n-butane dehydrogenation catalysts reported previously

(Table S6); derivation of the expressions of effective forward rate constants for n-butane dehydrogenation to butenes and n-butene dehydrogenation to 1,3-BD.

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Notes

The authors declare no competing financial interest.

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Reference:

1. Matar, S.; Hatch, L. F., Chemistry of petrochemical processes, 2nd Edition, *Elsevier*, **2001**.
2. Sun, Q. M.; Wang, N.; Fan, Q. Y.; Zeng, L.; Mayoral, A.; Miao, S.; Yang, R. O.; Jiang, Z.; Zhou, W.; Zhang, J. C.; Zhang, T. J.; Xu, J.; Zhang, P.; Cheng, J.; Yang, D. C.; Jia, R.; Li, L.; Zhang, Q. H.; Wang, Y.; Terasaki, O.; Yu, J. H., Subnanometer bimetallic platinum-zinc clusters in zeolites for propane dehydrogenation. *Angew. Chem. Int. Edit.* **2020**, *132*, 19618-19627.
3. Chen, S.; Zhao, Z.-J.; Mu, R.; Chang, X.; Luo, J.; Purdy, S. C.; Kropf, A. J.; Sun, G.; Pei, C.; Miller, J. T., Propane dehydrogenation on single-site [PtZn₄] intermetallic catalysts. *Chem* **2020**, *7*, 387-405.
4. Phadke, N. M.; Mansoor, E.; Bondil, M.; Head-Gordon, M.; Bell, A. T., Mechanism and kinetics of propane dehydrogenation and cracking over Ga/H-MFI prepared via vapor-phase exchange of H-MFI with GaCl₃. *J. Am. Chem. Soc.* **2019**, *141*, 1614-1627.
5. Searles, K.; Chan, K. W.; Burak, J. A. M.; Zemlyanov, D.; Safonova, O.; Coperet, C., Highly productive propane dehydrogenation catalyst using silica-supported Ga-Pt nanoparticles generated from single-sites. *J. Am. Chem. Soc.* **2018**, *140*, 11674-11679.
6. Sattler, J. J. H. B.; Ruiz-Martinez, J.; Santillan-Jimenez, E.; Weckhuysen, B. M., Catalytic dehydrogenation of light alkanes on metals and metal oxides. *Chem. Rev.* **2014**, *114*, 10613-10653.
7. Chen S.; Pei C.; Sun, G.; Zhao Z.-J.; Gong, J., Nanostructured catalysts toward efficient propane dehydrogenation. *Acc. Mater.s Res.* **2020**, *1*, 30-40.
8. Camacho-Bunquin, J.; Ferrandon, M. S.; Sohn, H.; Kropf, A. J.; Yang, C.; Wen, J.; Hackler, R. A.; Liu, C.; Celik, G.; Marshall, C. L., Atomically precise strategy to a PtZn alloy nanocluster catalyst for the deep dehydrogenation of n-butane to 1, 3-butadiene. *ACS Catal.* **2018**, *8*, 10058-10063.

9. Makshina, E. V.; Dusselier, M.; Janssens, W.; Degreve, J.; Jacobs, P. A.; Sels, B. F., Review of old chemistry and new catalytic advances in the on-purpose synthesis of butadiene. *Chem. Soc. Rev.* **2014**, *43*, 7917-7953.
10. White, W. C., Butadiene production process overview. *Chem.-Biol. Interact.* **2007**, *166*, 10-14.
11. Song, Y. J.; Liu, G. S.; Yuan, Z. Y., N-, P- and B-doped mesoporous carbons for direct dehydrogenation of propane. *RSC Adv.* **2016**, *6*, 94636-94642.
12. Estes, D. P.; Siddiqi, G.; Allouche, F.; Kovtunov, K. V.; Safonova, O. V.; Trigub, A. L.; Koptug, I. V.; Coperet, C., C-H activation on Co₂O sites: Isolated surface sites versus molecular analogs. *J. Am. Chem. Soc.* **2016**, *138*, 14987-14997.
13. Dai, Y. H.; Gu, J. J.; Tian, S. Y.; Wu, Y.; Chen, J. C.; Li, F. X.; Du, Y. H.; Peng, L. M.; Ding, W. P.; Yang, Y. H., γ -Al₂O₃ sheet-stabilized isolate Co²⁺ for catalytic propane dehydrogenation. *J. Catal.* **2020**, *381*, 482-492.
14. Chen, C.; Zhang, S. M.; Wang, Z.; Yuan, Z. Y., Ultrasmall Co confined in the silanols of dealuminated beta zeolite: A highly active and selective catalyst for direct dehydrogenation of propane to propylene. *J. Catal.* **2020**, *383*, 77-87.
15. Wang, G. W.; Zhang, H. L.; Wang, H. R.; Zhu, Q. Q.; Li, C. Y.; Shan, H. H., The role of metallic Sn species in catalytic dehydrogenation of propane: Active component rather than only promoter. *J. Catal.* **2016**, *344*, 606-608.
16. Wang, G. W.; Zhang, H. L.; Zhu, Q. Q.; Zhu, X. L.; Li, X. Y.; Wang, H.; Li, C. Y.; Shan, H. H., Sn-containing hexagonal mesoporous silica (HMS) for catalytic dehydrogenation of propane: An efficient strategy to enhance stability. *J. Catal.* **2017**, *351*, 90-94.
17. Searles, K.; Siddiqi, G.; Safonova, O. V.; Coperet, C., Silica-supported isolated gallium sites as highly active, selective and stable propane dehydrogenation catalysts. *Chem. Sci.* **2017**, *8*, 2661-2666.
18. Hu, B.; Schweitzer, N. M.; Zhang, G. H.; Kraft, S. J.; Childers, D. J.; Lanci, M. P.; Miller, J. T.; Hock, A. S., Isolated Fe-II on silica as a selective propane dehydrogenation catalyst. *ACS Catal.* **2015**, *5*, 3494-3503.
19. Maeno, Z.; Yasumura, S.; Wu, X. P.; Huang, M. W.; Liu, C.; Toyao, T.; Shimizu, K. I., Isolated indium hydrides in CHA zeolites: Speciation and catalysis for nonoxidative dehydrogenation of ethane. *J. Am. Chem. Soc.* **2020**, *142*, 4820-4832.
20. Xiong, C. Y.; Chen, S.; Yang, P. P.; Zha, S. J.; Zhao, Z. J.; Gong, J. L., Structure-performance relationships for propane dehydrogenation over aluminum supported vanadium oxide. *ACS Catal.* **2019**, *9*, 5816-5827.
21. Kong, N. N.; Fan, X.; Liu, F. F.; Wang, L.; Lin, H. P.; Li, Y. Y.; Lee, S. T., Single vanadium atoms anchored on graphitic carbon nitride as a high-performance catalyst for non-oxidative propane dehydrogenation. *ACS Nano* **2020**, *14*, 5772-5779.
22. Schweitzer, N. M.; Hu, B.; Das, U.; Kim, H.; Greeley, J.; Curtiss, L. A.; Stair, P. C.; Miller, J. T.; Hock, A. S., Propylene hydrogenation and propane dehydrogenation by a single-site Zn²⁺ on silica catalyst. *ACS Catal.* **2014**, *4*, 1091-1098.
23. Liu, G.; Zeng, L.; Zhao, Z. J.; Tian, H.; Wu, T. F.; Gong, J. L., Platinum-modified ZnO/Al₂O₃ for propane dehydrogenation: Minimized platinum usage and improved catalytic stability. *ACS Catal.* **2016**, *6*, 2158-2162.
24. Chen, C.; Hu, Z. P.; Ren, J. T.; Zhang, S. M.; Wang, Z.; Yuan, Z. Y., ZnO nanoclusters supported on dealuminated zeolite beta as a novel catalyst for direct dehydrogenation of propane to propylene. *ChemCatChem* **2019**, *11*, 868-877.

25. Camacho-Bunquin, J.; Aich, P.; Ferrandon, M.; Getsoian, A.; Das, U.; Dogan, F.; Curtiss, L. A.; Miller, J. T.; Marshall, C. L.; Hock, A. S.; Stair, P. C., Single-site zinc on silica catalysts for propylene hydrogenation and propane dehydrogenation: Synthesis and reactivity evaluation using an integrated atomic layer deposition-catalysis instrument. *J. Catal.* **2017**, *345*, 170-182.
26. Berndt, H.; Lietz, G.; Lucke, B.; Volter, J., Zinc promoted H-ZSM-5 catalysts for conversion of propane to aromatics .1. Acidity and activity. *Appl. Catal. A-Gen.* **1996**, *146*, 351-363.
27. Greenwood, N. N. E., A., Chemistry of the elements, 2nd ed. *Elsevier: Dordrecht, The Netherlands* **1997**.
28. Biscardi, J. A.; Iglesia, E., Structure and function of metal cations in light alkane reactions catalyzed by modified H-ZSM5. *Catal. Today* **1996**, *31*, 207-231.
29. Biscardi, J. A.; Iglesia, E., Non-oxidative reactions of propane on Zn/Na-ZSM5. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5753-5759.
30. Biscardi, J. A.; Meitzner, G. D.; Iglesia, E., Structure and density of active Zn species in Zn/H-ZSM5 propane aromatization catalysts. *J. Catal.* **1998**, *179*, 192-202.
31. Biscardi, J. A.; Iglesia, E., Reaction pathways and rate-determining steps in reactions of alkanes on H-ZSM5 and Zn/H-ZSM5 catalysts. *J. Catal.* **1999**, *182*, 117-128.
32. Niu, X. J.; Gao, J.; Miao, Q.; Dong, M.; Wang, G. F.; Fan, W. B.; Qin, Z. F.; Wang, J. G., Influence of preparation method on the performance of Zn-containing HZSM-5 catalysts in methanol-to-aromatics. *Microporous Mesoporous Mater.* **2014**, *197*, 252-261.
33. Ni, Y. M.; Sun, A. M.; Wu, X. L.; Hai, G. L.; Hu, J. L.; Li, T.; Li, G. X., The preparation of nano-sized H[Zn, Al]ZSM-5 zeolite and its application in the aromatization of methanol. *Microporous Mesoporous Mater.* **2011**, *143*, 435-442.
34. Fu, Z. H.; Yin, D. L.; Yang, Y. S.; Guo, X. X., Characterization of modified ZSM-5 catalysts for propane aromatization prepared by a solid-state reaction. *Appl. Catal. A-Gen.* **1995**, *124*, 59-71.
35. Tamiyakul, S.; Ubolcharoen, W.; Tungasmita, D. N.; Jongpatiwut, S., Conversion of glycerol to aromatic hydrocarbons over Zn-promoted HZSM-5 catalysts. *Catal. Today* **2015**, *256*, 325-335.
36. Almutairi, S. M. T.; Mezari, B.; Magusin, P. C. M. M.; Pidko, E. A.; Hensen, E. J. M., Structure and reactivity of Zn-modified ZSM-5 zeolites: The importance of clustered cationic Zn complexes. *ACS Catal.* **2012**, *2*, 71-83.
37. De Cola, P. L.; Glaser, R.; Weitkamp, J., Non-oxidative propane dehydrogenation over Pt-Zn-containing zeolites. *Appl. Catal. A-Gen.* **2006**, *306*, 85-97.
38. Gong, T.; Qin, L. J.; Lu, J.; Feng, H., ZnO modified ZSM-5 and Y zeolites fabricated by atomic layer deposition for propane conversion. *Phys. Chem. Chem. Phys.* **2016**, *18*, 601-614.
39. Nozik, D.; Tinga, F. M. P.; Bell, A. T., Propane dehydrogenation and cracking over Zn/H-MFI prepared by solid-state ion exchange of ZnCl₂. *ACS Catal.* **2021**, *11*, 14489-14506.
40. Yuan, Y.; Lobo, R. F., Zinc speciation and propane dehydrogenation in Zn/H-ZSM-5 catalysts. *ACS Catal.* **2023**, *13*, 4971-4984.
41. Zhao, D.; Tian, X.; Doronkin, D. E.; Han, S.; Kondratenko, V. A.; Grunwaldt, J.-D.; Perechodjuk, A.; Vuong, T. H.; Rabeah, J.; Eckelt, R., In situ formation of ZnO_x species for efficient propane dehydrogenation. *Nature* **2021**, *599*, 234-238.
42. Marques, J. P.; Gener, I.; Ayrault, P.; Bordado, J. C.; Lopes, J. M.; Ribeiro, F. R.; Guisnet, M., Dealumination of HBEA zeolite by steaming and acid leaching: distribution of the various aluminic species and identification of the hydroxyl groups. *C. R. Chim.* **2005**, *8*, 399-410.
43. Qi, L.; Zhang, Y.; Conrad, M. A.; Russell, C. K.; Miller, J.; Bell, A. T., Ethanol conversion

to butadiene over isolated zinc and yttrium sites grafted onto dealuminated Beta zeolite. *J. Am. Chem. Soc.* **2020**, *142*, 14674-14687.

44. Hammond, C.; Conrad, S.; Hermans, I., Simple and scalable preparation of highly active lewis acidic Sn- β . *Angew. Chem. Int. Edit.* **2012**, *51*, 11736-11739.

45. Zhang, Y.; Qi, L.; Lund, A.; Lu, P.; Bell, A. T., Mechanism and kinetics of acetone conversion to isobutene over isolated Hf sites grafted to Silicalite-1 and SiO₂. *J. Am. Chem. Soc.* **2021**, *143*, 8352-8366.

46. Kim, J.; Jentys, A.; Maier, S. M.; Lercher, J. A., Characterization of Fe-exchanged BEA zeolite under NH₃ selective catalytic reduction conditions. *J. Phys. Chem. C* **2013**, *117*, 986-993.

47. De'deck, J.; Tabor, E.; Sklenak, S., Tuning the aluminum distribution in zeolites to increase their performance in acid-catalyzed reactions. *ChemSusChem* **2019**, *12*, 556-576.

48. Bortnovsky, O.; Sobalik, Z.; Wichterlová, B., Exchange of Co (II) ions in H-BEA zeolites: Identification of aluminum pairs in the zeolite framework. *Microporous Mesoporous Mater.* **2001**, *46*, 265-275.

49. Kots, P. A.; Zabilska, A. V.; Ivanova, I. I., Selective self-condensation of butanal over Zr-BEA zeolites. *ChemCatChem* **2020**, *12*, 248-258.

50. Sushkevich, V. L.; Vimont, A.; Travert, A.; Ivanova, I. I., Spectroscopic evidence for open and closed Lewis acid sites in ZrBEA zeolites. *J. Phys. Chem. C* **2015**, *119*, 17633-17639.

51. Corma, A.; Fornes, V.; Forni, L.; Marquez, F.; Martinez-Triguero, J.; Moscotti, D., 2,6-Di-tert-butyl-pyridine as a probe molecule to measure external acidity of zeolites. *J. Catal.* **1998**, *179*, 451-458.

52. Gora-Marek, K.; Tarach, K.; Choi, M., 2, 6-Di-tert-butylpyridine sorption approach to quantify the external acidity in hierarchical zeolites. *J. Phys. Chem. C* **2014**, *118*, 12266-12274.

53. Hadjiivanov, K., Identification and characterization of surface hydroxyl groups by infrared spectroscopy. *Adv. Catal.* **2014**, *57*, 99-318.

54. Zhang, L.; Liang, Y.; Yu, L.; Wang, H.; Yin, M., Activating and modifying the basal planes of MoS₂ for superior NO₂ sensing at room temperature. *Sens. Actuators B-Chem.* **2022**, *359*, 131539.

55. Jiang, Q.; Wu, Z. Y.; Wang, Y. M.; Cao, Y.; Zhou, C. F.; Zhu, J. H., Fabrication of photoluminescent ZnO/SBA-15 through directly dispersing zinc nitrate into the as-prepared mesoporous silica occluded with template. *J. Mater. Chem.* **2006**, *16*, 1536-1542.

56. Rahman, I. A.; Padavettan, V., Synthesis of silica nanoparticles by sol-gel: Size-dependent properties, surface modification, and applications in silica-polymer nanocomposites-A review. *J. Nanomater.* **2012**, *2012*, 1-15.

57. Qasim, M.; Ananthaiah, J.; Dhara, S.; Paik, P.; Das, D., Synthesis and characterization of ultra-fine colloidal silica nanoparticles. *Adv. Sci. Eng. Med.* **2014**, *6*, 965-973.

58. Wang, L. G.; Sang, S. Y.; Meng, S. H.; Zhang, Y.; Qi, Y.; Liu, Z. M., Direct synthesis of Zn-ZSM-5 with novel morphology. *Mater. Lett.* **2007**, *61*, 1675-1678.

59. Zhang, Y. W.; Zhou, Y. M.; Huang, L.; Zhou, S. J.; Sheng, X. L.; Wang, Q. L.; Zhang, C., Structure and catalytic properties of the Zn-modified ZSM-5 supported platinum catalyst for propane dehydrogenation. *Chem. Eng J.* **2015**, *270*, 352-361.

60. Li, Y. W.; Bu, Y. Z.; Liu, Q.; Zhang, X.; Xu, J. L., High photocatalytic activities of zinc oxide nanotube arrays modified with tungsten trioxide nanoparticles. *Chinese J. Catal.* **2018**, *39*, 54-62.

61. Zhang, G.; Kim, G.; Choi, W., Visible light driven photocatalysis mediated via ligand-to-metal charge transfer (LMCT): an alternative approach to solar activation of titania. *Energ Environ. Sci.* **2014**,

7, 954-966.

62. Qi, L.; Babucci, M.; Zhang, Y.; Lund, A.; Liu, L.; Li, J.; Chen, Y.; Hoffman, A. S.; Bare, S. R.; Han, Y.; Gates, B. C.; Bell, A. T., Propane dehydrogenation catalyzed by isolated Pt atoms in $\equiv\text{SiOZn-OH}$ nests in dealuminated zeolite Beta. *J. Am. Chem. Soc.* **2021**, *143*, 21364-21378.
63. Zhu, Q.; Wang, G.; Zhang, H.; Zhu, X.; Li, C., n-Butane dehydrogenation over Ni-Sn/SiO₂: Adsorption modes and reaction paths of n-butane and 1-butene. *Appl. Catal. A-Gen.* **2018**, *566*, 113-120.
64. Deng, L.; Miura, H.; Ohkubo, T.; Shishido, T.; Wang, Z.; Hosokawa, S.; Teramura, K.; Tanaka, T., The importance of direct reduction in the synthesis of highly active Pt-Sn/SBA-15 for n-butane dehydrogenation. *Catal. Sci. Technol.* **2019**, *9*, 947-956.
65. Wu, J.; Peng, Z.; Sun, P.; Bell, A. T., n-Butane dehydrogenation over Pt/Mg (In)(Al) O. *Appl. Catal. A-Gen.* **2014**, *470*, 208-214.
66. Yi, F.; Chen, H.; Huang, L.; Hu, C.; Wang, J.; Li, T.; Wang, H.; Tao, Z.; Yang, Y.; Li, Y., Effects of the acidity and shape selectivity of dealuminated zeolite beta on butene transformations. *Fuel* **2021**, *300*, 120694-120707.
67. Phadke, N. M.; Mansoor, E.; Head-Gordon, M.; Bell, A. T., Mechanism and Kinetics of Light Alkane Dehydrogenation and Cracking over Isolated Ga Species in Ga/H-MFI. *ACS Catal.* **2021**, *11*, 2062-2075.
68. Kopač, D.; Jurković, D. L. i.; Likožar, B.; Huš, M., First-principles-based multiscale modelling of nonoxidative butane dehydrogenation on Cr₂O₃ (0001). *ACS Catal.* **2020**, *10*, 14732-14746.
69. Chang, C.; Conner, W.; Kokes, R., Butene isomerization over zinc oxide and chromia. *J. Phys. Chem.* **1973**, *77*, 1957-1964.
70. Fang, H.; Zheng, A.; Xu, J.; Li, S.; Chu, Y.; Chen, L.; Deng, F., Theoretical investigation of the effects of the zeolite framework on the stability of carbenium ions. *J. Phys. Chem. C* **2011**, *115*, 7429-7439.
71. Wang, J.; Hokkanen, B.; Burghaus, U., Adsorption of iso-butane on ZnO(0001)-Zn. *Surf. Sci.* **2006**, *600*, 4855-4859.
72. Zhang, Y.; Qi, L.; Leonhardt, B.; Bell, A. T., Mechanism and kinetics of n-butane Dehydrogenation to 1, 3-Butadiene Catalyzed by Isolated Pt Sites Grafted onto $\equiv\text{SiOZn-OH}$ Nests in Dealuminated Zeolite Beta. *ACS Catal.* **2022**, *12*, 3333-3345.
73. Qi, L.; Zhang, Y.; Babucci, M.; Chen, C.; Lu, P.; Li, J.; Dun, C.; Hoffman, A. S.; Urban, J. J.; Tsapatsis, M.; Bare, S. R.; Han, Y.; Gates, B. C.; Bell, A. T., Dehydrogenation of propane and n-butane catalyzed by isolated PtZn₄ sites supported on self-pillared pentasil nanosheets. *ACS Catal.* **2022**, *12*, 11177-11189.
73. Xie, L.; Wang, R.; Chai, Y.; Weng, X.; Guan, N.; Li, L., Propane dehydrogenation catalyzed by in-situ partially reduced zinc cations confined in zeolites. *J. Energy Chem.* **2021**, *63*, 262-269.

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