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Article

# Interpretation of H<sub>2</sub>-TPR from Cu-CHA Using First-Principles Calculations

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**ABSTRACT:** Temperature-programmed reduction and oxidation are used to obtain information on the presence and abundance of different species in complex catalytic materials. The interpretation of the temperature-programmed reaction profiles is, however, often challenging. One example is H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) of Cu-chabazite (Cu-CHA), which is a material used for ammonia assisted selective catalytic reduction of NO<sub>x</sub> (NH<sub>3</sub>-SCR). The TPR profiles of Cu-CHA consist generally of three main peaks. A peak at 220 °C is commonly assigned to ZCuOH, whereas peaks at 360 and 500 °C generally are assigned to Z<sub>2</sub>Cu, where Z represents an Al site. Here, we analyze H<sub>2</sub>-TPR over Cu-CHA by density functional theory calculations, micro-



kinetic modeling, and TPR measurements of samples pretreated to have a dominant Cu species. We find that  $H_2$  can react with Cu ions in oxidation state +2, whereas adsorption on Cu ions in +1 is endothermic. Kinetic modeling of the TPR profiles suggests that the 220 °C peak can be assigned to  $Z_2$ CuOCu and ZCuOH, whereas the peaks at higher temperatures can be assigned to paired  $Z_2$ Cu and  $Z_2$ CuHOOHCu species (360 °C) or paired  $Z_2$ Cu and  $Z_2$ CuOOCu (500 °C). The results are in good agreement with the experiments and facilitate the interpretation of future TPR experiments.

# INTRODUCTION

Temperature-programmed reduction with  $H_2$  ( $H_2$ -TPR) is widely used in heterogeneous catalysis to characterize materials.<sup>1</sup> The method is straightforward and works by flowing  $H_2$  over a catalyst, while gradually increasing the temperature. By measuring the consumption of  $H_2$  during the temperature ramp, information on the chemistry and reducibility of the catalyst material is obtained. The TPR profiles are, however, often complex with many overlapping features, which makes the interpretation ambiguous.

H<sub>2</sub>-TPR has been extensively used to characterize copperfunctionalized zeolites to describe and quantify different Cu species.<sup>2–12</sup> The copper-exchanged small pore zeolite chabazite (Cu-CHA) is used for several important applications. Cu-CHA is presently a state-of-the-art catalyst for deNOx by ammonia-assisted selective catalytic reduction (NH<sub>3</sub>–SCR) in diesel-aftertreatment systems.<sup>13–16</sup> Furthermore, Cu-CHA has been explored for one-step conversion of methane to methanol.<sup>17–19</sup>

The assignment of Cu species from H<sub>2</sub>-TPR in Cu-CHA is challenging as H<sub>2</sub> consumption depends on the detailed composition of the catalyst (Si/Al ratio and Cu loading), synthesis method, the oxidation state of Cu (Cu<sup>I</sup> or Cu<sup>II</sup>), location of Cu ions (e.g., 6- or 8-membered rings), and ligands bound to Cu.<sup>2–5,20</sup> An additional complication is the dynamic character of the Cu species, which is known to depend critically on the pretreatment of the catalyst. For example,

exposure of the catalyst to NH<sub>3</sub> at low temperature results in the formation of mobile  $[Cu(NH_3)_x]^+$  ( $x \ge 2$ ) complexes,<sup>21–24</sup> and O<sub>2</sub> adsorption on the NH<sub>3</sub>-solvated complexes yields peroxo complexes  $[Cu_2(NH_3)_4O_2]^{2+}$ .  $[Cu(NH_3)_2]^+$  and  $[Cu_2(NH_3)_4O_2]^{2+}$  have been suggested to be important for the low-temperature NH<sub>3</sub>-SCR reaction.<sup>25–27</sup> The NH<sub>3</sub> ligands desorb at high temperatures yielding framework-bound Cu species where ZCuOH and Z<sub>2</sub>Cu are two examples.<sup>28</sup> Here Z denotes the Al environment with Z being a one-Al environment and Z<sub>2</sub> being a two-Al environment.

H<sub>2</sub>-TPR peaks for Cu-CHA are commonly observed at ~220, ~360, and ~500 °C;<sup>2-4,6,10-12</sup> however, the assignments of these peaks are conflicting. The low-temperature peak at 220 °C is often assigned to reduction of ZCuOH species;<sup>3,6,10</sup> however, peaks at similar temperatures have also been assigned to the reduction of CuO clusters.<sup>5,12</sup> The assignments of the two peaks at 360 and 500 °C are more challenging, and the peaks are not always present in the TPR profile.<sup>2,3,6</sup> The peak at 360 °C has been suggested to be the

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reduction of either ZCuOH or  $Z_2$ Cu.<sup>6,10,12</sup> The peak at 500 °C is typically assigned to  $Z_2$ Cu.<sup>10,12</sup> Moreover, it has also been suggested that both the 360 and the 500 °C peaks are related to  $Z_2$ Cu with different atomic structures<sup>10</sup> or, alternatively, pristine or hydrated  $Z_2$ Cu.<sup>6</sup> H<sub>2</sub>-TPR peaks are sometimes observed also at very high temperatures (>800 °C) and are in this case related to the formation of metallic Cu.<sup>3,4</sup> It should be noted that the comparison of the H<sub>2</sub>-TPR profiles between different studies is difficult as the H<sub>2</sub> consumption depends on the Si/Al ratio (SAR), Cu loading, and sample pretreatment.<sup>2,3,6</sup> Because of the dynamic character of the Cu species, the actual Cu species present in the investigated samples depends sensitively on the history of the samples.

The interpretation of the H<sub>2</sub>-TPR profiles is important as it often is used to develop atomic-level understanding of the catalytic reaction. For example, conclusions regarding the H<sub>2</sub>-TPR profiles have been used to quantify the ratio between ZCuOH and Z<sub>2</sub>Cu species to understand trends in hydro-thermal stability<sup>29</sup> and sulfur poisoning.<sup>6</sup> The H<sub>2</sub>-TPR determined ratio between ZCuOH and Z<sub>2</sub>Cu has, moreover, been used as input data for reactor models of Cu-CHA.<sup>30</sup>

Although  $H_2$ -TPR has been used extensively on Cu-CHA, there is an ambiguity as to which Cu species that are responsible for the  $H_2$  consumption, and the use of the technique to make structure–function links is currently hampered by the lack of chemical understanding of the active sites for  $H_2$ -TPR.

Herein we use density functional theory (DFT) and microkinetic modeling in combination with TPR measurements to study the reaction of  $H_2$  with different Cu species. The DFT calculations are performed for a range of Cu species known to be present in Cu-CHA. The DFT results are used to construct a microkinetic model to simulate the  $H_2$ -TPR profiles. We study both NH<sub>3</sub>-solvated Cu species, which are relevant for low-temperature NH<sub>3</sub>-SCR and framework-bound species, which are present during high-temperature operation. The experiments are performed by preparing solvated and framework bound Cu species as well as Cu species formed during SCR conditions. The study shows that combining DFTbased microkinetic modeling and  $H_2$ -TPR measurements offers detailed knowledge of the Cu-CHA material, which enables a link between structural properties and catalyst function.

#### THEORETICAL AND EXPERIMENTAL METHODS

DFT Calculations. Spin-polarized density functional theory calculations are performed with the Vienna Ab initio Simulation Package (VASP),  $^{31,32}$  version 5.4.4. The Kohn– Sham orbitals are expanded with plane waves using a cutoff value of 480 eV. The interaction between the valence electrons and the core is described with the plane augmented wave (PAW) method.<sup>33,34</sup> The valence electrons considered for each atom are Cu(11), Si(4), Al(3), O(6), N(5), and H(1). The exchange-correlation term is approximated using the Perdew-Burke-Ernzerhof (PBE) functional.<sup>35</sup> The PBE functional is augmented with a Hubbard-U term for Cu 3d to describe the localization of these orbitals,<sup>36</sup> and a correction<sup>37</sup> is added to describe the weak van der Waals forces for species in the zeolite. The converging criteria for the SCF loop is set to  $10^{-5}$ eV. The structures are considered to be at a minimum if the norm of all forces acting on the atoms is less than 0.02 eV/Å. Climbing image nudged elastic band (CI-NEB)<sup>38,39</sup> is used to locate the transition states, which are confirmed by vibrational analyses. The vibrational analysis is performed using the finite

difference method. The reaction landscapes are reported with zero-point corrections. Bader charge analyses are performed using the implementation by Henkelmann and co-workers.<sup>40,41</sup> To explore the flat energy landscape, ab initio molecular dynamic (AIMD) simulations are performed and structures along the trajectory are relaxed. The temperature is set to 300 K and is controlled by a Nosé–Hoover thermostat<sup>42,43</sup> in the NVT ensemble. A hexagonal unit cell consisting of 36 Si and 72 O atoms is used to model the CHA zeolite. The system is treated with a Si/Al ratio between 5 and 35. The Al site is charged compensated by either H or Cu.

**Simulation of H<sub>2</sub>-TPR.** We construct a microkinetic model to simulate the kinetics of the studied  $H_2$  reactions during a temperature ramp. In the microkinetic model, a set of coupled differential equations are solved.

$$\frac{\mathrm{d}\theta_i}{\mathrm{d}t} = \sum_j v_{ij} r_j \tag{1}$$

 $\theta_i$  is the fractional coverage of species *i*,  $v_{ij}$  is the stoichiometry coefficient for species *i* and reaction *j*, and  $r_j$  is the rate of reaction *j*. The coupled differential equations are solved numerically in Python using the solve\_ivp command from the scipy.integrate package, with the implicit multistep variable-order (BDF) method. In temperature-programmed desorption (TPD), the time-dependent rate of desorption for species *i* ( $r_{des}$ ) is described by<sup>44</sup>

$$r_{\rm des}(t) = k_{\rm des}^{i}(t)\theta_{i}(t) = -\frac{\mathrm{d}\theta_{i}(t)}{\mathrm{d}t}$$
(2)

The rate of desorption  $r_{\text{des}}$  depends on the rate constant  $k_{\text{des}}^{i}$  and the fractional coverage of the adsorbed species  $\theta_{i}$ . The temperature of the system is a function of time (t):

$$T = T_0 + \beta t \tag{3}$$

Here,  $T_0$  is the starting temperature and  $\beta$  is the heating rate. Equation 2 can be adopted to TPR measurements,<sup>45</sup> where instead the consumption (adsorption) of H<sub>2</sub> is monitored:

$$r_{\rm ads}(t) = k_{\rm ads}^{i}(t)\theta_{i}(t) = \frac{\mathrm{d}\theta_{i}(t)}{\mathrm{d}t}$$
(4)

For TPR, the rate constant of the adsorption  $(k_{ads}^i(t))$  is used instead of  $r_{des}$ . The rate constants are computed from transition state theory (TST).

$$k = \frac{k_{\rm B}T}{h} e^{-\Delta G/k_{\rm B}T} = \frac{k_{\rm B}T}{h} e^{\Delta S/k_{\rm B}} e^{-\Delta H/k_{\rm B}T}$$
$$\approx \frac{k_{\rm B}T}{h} e^{\Delta S/k_{\rm B}} e^{-\Delta E/k_{\rm B}T}$$
(5)

 $k_{\rm B}$  is the Boltzmann constant, *T* is temperature, *h* is Planck's constant, and  $\Delta G$  is the change in the Gibbs free energy between the transition state and the initial state. The enthalpy is approximated as the zero point corrected DFT energy, *E*. For adsorbed H<sub>2</sub>, the entropy is evaluated via the vibrational partition function, and for gas phase H<sub>2</sub>, the entropy is evaluated via the partition, translation, and rotation. For the dissociative adsorption of H<sub>2</sub>, the rate constant is described by collision theory.

$$k = \frac{pA}{(2\pi m k_{\rm B}T)^{1/2}} e^{-\Delta E/k_{\rm B}T}$$
(6)



**Figure 1.**  $H_2$ -TPR test protocols for four different copper states and comparison of the hydrated and dehydrated conditions over the Cu-CHA. The TPR experiments examines (a) mobile diamine complex, (b) oxidized mobile diamine complex, (c) framework bound Cu<sup>I</sup>, (d) oxidized framework bound Cu<sup>II</sup>, (e) hydrated condition, and (f) dehydrated condition. Total flow rate: 20 N mL/min; heating rate: 10 °C/min.



Figure 2. Considered Cu species: (1)  $[Cu(NH_3)_2]^+$ , (2)  $[Cu_2(NH_3)_4O_2]^{2+}$ , (3) ZCu, (4)  $Z_2Cu_2$ , (5)  $Z_2Cu$ , (6) paired  $Z_2Cu$ , (7) ZCuOH, (8)  $Z_2CuOOCu$ , (9)  $Z_2CuHOOHCu$ , and (10)  $Z_2CuOCu$ . For configurations not bonded to the framework (a and b), the cage is not shown for clarity. Atomic color codes: H (white), N (blue), O (red), S (yellow), and Cu (bronze).

*p* is the partial pressure, *A* is the area, which is set to the pore size of the zeolite corresponding to the eight-membered ring, *m* is the mass, and  $\Delta E$  is the change in zero-point corrected DFT energy between the transition state and initial state. To

ensure thermodynamic consistency, the desorption rate,  $k_{des}$ , is

calculated from the equilibrium constant, K.

$$K = \frac{k_{\rm ads}}{k_{\rm des}} = e^{-\Delta G/k_{\rm B}T}$$
<sup>(7)</sup>

The desorption of  $H_2O$  is modeled as an irreversible reaction with the following rate constant.

$$k_{\rm des} = A e^{-E_{\rm ads}/k_{\rm B}T} \tag{8}$$

 $E_{\rm ads}$  is the zero-point corrected desorption energy, and the prefactor for the desorption is set to  $10^{12} \text{ s}^{-1}$ .

Cu-CHA Synthesis. A Cu-CHA powder is prepared by first synthesizing a Na form of CHA (Na-CHA) using a direct hydrothermal synthesis method. In a second step, an NH<sub>4</sub> form of CHA (NH<sub>4</sub>-CHA) is prepared using an ion-exchange method with ammonium nitrate  $(NH_4NO_3)$ . A detailed account of the synthesis procedure is reported elsewhere.<sup>2,12,46</sup> The NH<sub>4</sub>-CHA powder is used to prepare the Cu<sup>II</sup>-exchanged CHA (Cu-CHA) powder using the incipient wetness impregnation method. 0.160 g of copper nitrate  $(Cu(NO_3)_2)$ . 2.5H<sub>2</sub>O, Sigma-Aldrich, pentahydrate) is dissolved into 3 g of ethanol as a mixture. 2 g of the prepared NH<sub>4</sub>-CHA powder is introduced into the copper-containing mixture, and the resulting mixture is continuously stirred for 15 min. Subsequently, the mixture is dried at room temperature overnight and thereafter well-crushed to a fine powder form. The crushed Cu-CHA powder is calcined at 600 °C for 8 h, followed by 750 °C for 2 h at a heating rate of 2 °C/min. Elemental composition of the Cu-CHA powder is analyzed through an inductively coupled plasma mass spectrometry (ICP) analysis for Si, Al, and Cu. The ICP results show an Si/ Al ratio = 11.4 and 2 wt % Cu.

Temperature-Programmed Reduction with H<sub>2</sub>. Temperature-programmed reduction with H<sub>2</sub> (H<sub>2</sub>-TPR) is performed with the prepared Cu-CHA sample. Prior to the test, the sample is exposed to standard SCR conditions (400 ppm of NH<sub>3</sub>/NO, 5% H<sub>2</sub>O, 10% O<sub>2</sub>, Ar Bal.) at 750 °C for 5 h to degreen the Cu-CHA powder. Thereafter, the resulting Cu-CHA powder is sieved to obtain a narrower particle size range (180–250  $\mu$ m). The resulting Cu-CHA sample is loaded inside a vertical quartz tube within a differential scanning calorimeter (Sensys DSC calorimeter, Setaram).

The samples are pretreated to obtain six dominant types of copper species following the  $H_2$ -TPR test protocols in Figure 1.

Initially, five of the samples were pretreated at 500 °C under oxidizing conditions  $(10\% O_2)$  for 30 min, which would remove most of the water for the samples as well as oxidize the copper. In the first experiment the mobile diamine complex is targeted (Figure 1a). This is done by exposing the Cu-CHA sample to 2400 ppm of NH<sub>3</sub> + 2000 ppm of NO through reduction half-cycle according to the standard SCR mechanism at low temperature.<sup>47,48</sup> Thereafter, the oxidized mobile diamine complex is examined (Figure 1b) by exposing the mobile diamine complex to O2 at 200 °C for 40 min. The diamine complex efficiently activates  $O_2$  molecule at 200 °C, leading to the oxidized mobile diamine complex (Figure 2b).47 The method shown in Figure 1c focuses on the framework bound Cu<sup>I</sup> and the oxidized framework bound Cu<sup>II</sup> (Figure 1d) by treating the mobile diamine complex to high temperature at 500 °C for 1 h. Under the thermal treatment, NH<sub>3</sub> desorbs from the complex leading to the framework bounded Cu<sup>I,47</sup> The resulting framework bound Cu<sup>I</sup> activates the O<sub>2</sub> molecule at 200 °C, leading to the framework bound Cu<sup>II</sup>.<sup>47</sup> Figures 1c and 1d therefore lead to framework bound

Cu<sup>I</sup> and Cu<sup>II</sup>, respectively. The degreened Cu-CHA powder is exposed to air for several days to allow for water uptake to mimic hydrated conditions as shown in Figure 1e to identify ZCuOH at low temperature by comparing dry conditions (Figure 1f). The mobile diamine complexes, oxidized mobile diamine complexes, and framework-bound Cu<sup>I</sup> species have previously been identified using X-ray absorption spectroscopy on Cu-CHA samples exposed to similar pretreatments as in the present study.<sup>21,22,49,50</sup>

After each pretreatment, the temperature is cooled to room temperature. The H<sub>2</sub>-TPR is started by exposing the sample to 2000 ppm of H<sub>2</sub> at RT for 30 min and a temperature ramp where the temperature is increased to 800 °C at heating rate of 10 °C/min. The temperature is thereafter kept at 800 °C for 30 min. Effluent gases are monitored with a mass spectrometer (Hiden HPR-20 QUI MS) for H<sub>2</sub> (m/e = 2), NH<sub>3</sub> (15), H<sub>2</sub>O (18), Ar (20), N<sub>2</sub> (28), NO (30), O<sub>2</sub> (32), N<sub>2</sub>O (44), and NO<sub>2</sub> (46). Ar is used as a balance gas, and the total flow rate was maintained at 20 N mL/min during the entire measurements.

#### RESULTS

Considered Cu Species. The state of the Cu ions in Cu-CHA depends sensitively on the reaction conditions.<sup>21</sup> Here we consider the structures shown in Figure 2. At lowtemperature NH<sub>3</sub>-SCR conditions, the Cu ions are solvated, forming mobile  $[Cu^{I}(NH_{3})_{2}]^{+}$  complexes (structure (1)).<sup>21-</sup> A pair of mobile complexes can react with O<sub>2</sub>, forming peroxo complexes  $[Cu_2^{II}(NH_3)_4O_2]^{2+}$  (structure (2)). Structures (1) and (2) are important intermediates in the low-temperature NH<sub>3</sub>-SCR reaction.<sup>25–27</sup> At higher temperatures, NH<sub>3</sub> desorbs, and the Cu ions bind to the zeolite framework, forming, for example, structures (3) and (4). (3) is a single Cu<sup>I</sup> ion in the six-membered ring, whereas (4) is paired Cu<sup>I</sup> ions balanced by two Al sites. The Cu configurations  $Z_2Cu^{II}$  (structures (5) and (6)) and  $ZCu^{II}OH$  (structure (7)) are structures frequently discussed in the literature.<sup>2,3,6</sup> (5) is an isolated  $Cu^{II}$  ion located in a six-membered ring, and (6) are paired  $Cu^{II}$  ions located in six-membered rings. The ZCu<sup>II</sup>OH species in structure (7) is located in the eight-membered ring. If the catalyst is exposed to  $O_2$  at high temperature, a pair of Cu ions may adsorb an oxygen molecule, forming a framework bound peroxo species  $Z_2Cu^{II}OOCu^{II}$  (structure (8)) in an eight-membered ring.<sup>47</sup> Structure (8) has been suggested to be important for the methane-to-methanol reaction.<sup>17,18</sup> Structure (9)  $(Z_2Cu^{II}HOOHCu^{II})$  and structure (10)  $(Z_2Cu^{II}OCu^{II})$  are two additional structures in the eight-membered ring that have been proposed to be present in Cu-CHA.<sup>17-19</sup> (9) could potentially be formed by the reaction of two ZCu<sup>II</sup>OH complexes.

 $H_2$  Adsorption over Cu Species in Cu-CHA. The potential energy diagrams for  $H_2$  adsorption over the different types of Cu species are presented in Figures 3 and 4. We did not find it possible to adsorb or dissociate  $H_2$  over structure (1) ([Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>); thus, we do not expect this complex to consume  $H_2$  during TPR measurements.

The peroxo complex  $[Cu_2(NH_3)_4O_2]^{2+}$  (structure (2)) is flexible, and we were not able to locate a transition state for H<sub>2</sub> dissociation using CI-NEB. Instead, constrained AIMD simulations were performed to probe the reaction barrier. The simulation is shown in Figure 3. The collective variable is the sum of the bond lengths between the hydrogen atoms and the Cu (see the Supporting Information for more informa-



**Figure 3.** Constrained AIMD simulations of the energy profile for the reaction of  $H_2$  with the mobile peroxo dimer  $[Cu_2(NH_3)_4O_2]^{2+}$ . The gray line is the energy, and the red line is the rolling average of the energy. Atomic color codes as in Figure 2.

tion). The energy barrier for  $H_2$  adsorption is 0.92 eV.  $H_2$  dissociates over a Z site before forming  $H_2O$  in the final state. The Cu ions are in a +2 oxidation state in both the initial and final states, and the two oxygen atoms are reduced ( $O^{1-} \Rightarrow O^{2-}$ ). Reacting a second  $H_2$  molecule with the remaining oxygen atom leads to a pair of  $[Cu(H_2O)(NH_3)_2]^+$  complexes with Cu in the oxidation state +1 (see the Supporting Information).

The potential energy diagrams for  $H_2$  adsorption and dissociation over the Cu species are collected in Figure 4. Four different Cu species are considered for the framework-bound Cu complexes without extraframework oxygen ligands, namely isolated (structure (3)) and paired ZCu (structure (4)) and isolated Z<sub>2</sub>Cu (structure (5)) and paired Z<sub>2</sub>Cu (structure (6)). The results for isolated ZCu (structure (3)) is shown in the Supporting Information. H<sub>2</sub> adsorbs weakly on isolated ZCu (-0.28 eV), and the subsequent reactions are highly endothermic.

A pair of ZCu (structure (4)) can dissociate H<sub>2</sub>, and the reaction landscape for the reaction is shown in Figure 4. To dissociate H<sub>2</sub>, the Cu ions diffuse to form a Cu pair. The starting structure 2Cu corresponds to two ZCu ions located in an eight- and six-membered ring. The first step involves diffusion of the Cu ion in the eight-membered ring to an adjacent eight-membered ring forming structure 2Cu\*. The diffusion is endothermic by 0.22 eV and associated with a barrier of 0.57 eV. The next step, which is the formation of the final Cu pair, is endothermic by 0.55 eV with a Cu-Cu distance of 2.5 Å (structure Cu-Pair). The short distance between the two Cu ions is necessary to dissociate H<sub>2</sub>. H<sub>2</sub> adsorbs on one of the Cu ions with a binding energy of -0.72eV forming Z<sub>2</sub>CuH<sub>2</sub>Cu. H<sub>2</sub> dissociates over the pair with a barrier of 0.26 eV, forming Z<sub>2</sub>CuHHCu. In this structure, the Cu ions remain in a +1 oxidation state, and the hydrogen atoms remain neutral. One of the hydrogen atoms can migrate to a Brønsted site forming Z<sub>2</sub>Cu-H-Cu + ZH, where ZH denotes the Brønsted acid site. The next step is the simultaneous reduction of the Cu ions into a Cu dimer and two Brønsted acid sites ( $Cu_2 + 2ZH$ ). This leads to two Brønsted acid sites and a Cu<sub>2</sub> dimer with a bond length of 2.24 Å. The reduction has a high barrier of 1.52 eV and is endothermic by 1.51 eV. The reaction landscape for H<sub>2</sub> adsorption and dissociation over two ZCu suggests that this reaction is unfavorable. ZCu have been reported to be reduced

at high temperatures<sup>3</sup> and associated with the destruction of the framework,<sup>4</sup> a process that we have not considered here.

For isolated  $Z_2Cu$  (structure (5)), the dissociation of  $H_2$ , results in a Cu–H complex and a Brønsted acid site (ZCuH + ZH). The barrier is 0.51 eV, and the reaction is endothermic by 0.35 eV; thus this reaction is not favored. The Cu ion in structure ZCuH + ZH has a magnetic moment of 0.47, which implies that the Cu ion remains in a +2 oxidation state. This is corroborated by a Bader charge analysis, showing that the charge on the Cu ion changes from +1.17*e* to +0.90*e* in the reaction. The hydrogen atom bound to the Cu ion is slightly negatively charged (-0.28*e*), and the hydrogen atom bound to the Brønsted site has a positive charge (+0.59*e*). Thus, the Cu ion remains in the +2 oxidation state because of the formation of a formal H<sup>-</sup> ion.

An alternative route for the reaction of H<sub>2</sub> with Z<sub>2</sub>Cu, is the reaction of one H<sub>2</sub> molecule over paired Z<sub>2</sub>Cu sites (structure (6)), forming 2ZCu + 2ZH. H<sub>2</sub> dissociates over Cu forming  $Z_2Cu + ZHZCuH$ , which is the same step as for isolated  $Z_2Cu$ . The dissociation of H<sub>2</sub> is endothermic by 0.56 eV and has a barrier of 0.8 eV. One of the hydrogen atoms can migrate from Cu to a Brønsted site (2ZCu + 2ZH). The two Cu ions are reduced to Cu<sup>I</sup> upon the hydrogen diffusion. The hydrogen diffusion has a large barrier of 1.32 eV, and the reaction is exothermic by -0.79 eV. In this 2ZCu + 2ZH configuration, 2 Al ions are associated with two Brønsted acid sites and a Cu ion, thus, a local structure that is not fully charge stabilized. Hydrogen diffusion to a nearby Al ion stabilizes the local charge. This second diffusion step has a barrier of 0.62 eV and is exothermic by -0.4 eV. Further diffusion of the hydrogen leads to more stable structure. First, the hydrogen can rotate lowering the energy by -0.11 eV. The last step is hydrogen diffusion to an oxygen in the six-membered ring, lowering the energy by -0.08 eV with a barrier of 0.58 eV.

Turning to the oxygen-containing Cu species, we start with  $H_2$  reacting with ZCuOH (structure (7)).  $H_2$  dissociates over the Cu ion forming a Cu–H complex with  $H_2O$  bound to the Cu ion (structure ZCuH– $H_2O$ ). The barrier is 0.52 eV, and the reaction is exothermic by -0.25 eV. The Cu ion in ZCuOH remains in a +2 oxidation state, and the hydrogen bound to Cu is slightly negatively charged (-0.18*e*), which is similar to the Z<sub>2</sub>Cu case. The formed  $H_2O$  has a desorption energy of 0.95 eV forming ZCuH. As the hydrogen atom is negatively charged, it can, in principle, be transferred in an exothermic reaction to another ZCuOH complex forming an  $H_2O$  molecule and two ZCu ions. Thus, paired ZCuOH sites can be reduced by a single hydrogen molecule  $H_2$  (reaction landscape in the Supporting Information).

An  $O_2$  molecule can adsorb on a pair of Cu ions forming a framework-bound peroxo species,<sup>47</sup> Z<sub>2</sub>CuOOCu (structure (8)). H<sub>2</sub> does not dissociate directly over the oxygen atoms. However, similar to the previous reaction landscapes, H<sub>2</sub> dissociates over the Cu ions. The dissociation of H<sub>2</sub> is endothermic by 1.0 eV and results in a Z<sub>2</sub>CuHHOOCu species. Both Cu ions remain in a +2 oxidation state. The hydrogen atom bound to the Cu ion is slightly negatively charged by -0.18*e*, whereas the hydrogen bound to the oxygen atom is positively charged (+0.65*e*). This charge separation is similar to H<sub>2</sub> over ZCuOH and Z<sub>2</sub>Cu. In a subsequent exothermic step (-3.5 eV), the hydrogen atom bound to the Cu ion migrates to the oxygen (Z<sub>2</sub>CuHOCuOH), reducing the two oxygen atoms (O<sup>1-</sup>  $\Rightarrow$  O<sup>2-</sup>) The free -OH group can

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Figure 4. Reaction landscape for the dissociation of  $H_2$  over (4)  $Z_2Cu_2$ , (5)  $Z_2Cu$ , (6) paired  $Z_2Cu$ , (7) ZCuOH, (8)  $Z_2CuOOCu$ , (9)  $Z_2CuHOOHCu$ , and (10)  $Z_2CuOCu$ . Atomic color codes as in Figure 2.

bind to the Cu ion forming a very stable  $Z_2CuHOOHCu$  species (exothermic by -1.16 eV) with a barrier of 0.12 eV.

The formed Z<sub>2</sub>CuHOOHCu species can react further with an additional H<sub>2</sub> (structure (9)). The Z<sub>2</sub>CuHOOHCu species could also be formed by the reaction of two ZCuOH species (see reaction path in the Supporting Information). H<sub>2</sub> does not adsorb over Z<sub>2</sub>CuHOOHCu, and the reaction can proceed only after the formation of a Z<sub>2</sub>CuOCuH<sub>2</sub>O species. Z<sub>2</sub>CuOCuH<sub>2</sub>O is formed by breaking a Cu–O bond to form an –OH group bound to a single Cu (Z<sub>2</sub>CuOHCuOH). This reaction step is highly endothermic (1.5 eV). In a next step, the hydrogen atom is transferred to the –OH group in a thermoneutral reaction with a barrier of 0.05 eV. The desorption of H<sub>2</sub>O is associated with a barrier of 0.4 eV forming  $Z_2CuOCu$ . The reaction of  $Z_2CuOCu$  with  $H_2$  follows the same path for structure (10).

 $Z_2$ CuOCu complexes have also been proposed to exist and formed from the dehydration of  $Z_2$ CuHOOHCu species (structure (10)).  $H_2$  is in this case dissociated over a Cu ion with a barrier of 0.55 eV forming  $Z_2$ CuOHCuH. The hydrogen atoms can subsequently migrate to the –OH group forming  $H_2O$ , ( $Z_2$ CuH<sub>2</sub>OCu) in an exothermic reaction, whereby the Cu ion is reduced to a +1 oxidation state. The  $H_2O$  molecule is bound to both Cu ions with a Cu–O bond length of 2.00 Å. The desorption energy of  $H_2O$  from this state is 1.85 eV; hence  $H_2O$  is strongly bonded. The DFT calculations suggest that only ions in oxidation state +2 are expected to be reduced to +1 upon  $H_2$  exposure. **Simulated H<sub>2</sub>-TPR Profiles.** The DFT calculations show that neither the mobile  $[Cu(NH_3)_2]^+$  complex nor the framework-bound ZCu adsorbs H<sub>2</sub>. H<sub>2</sub> adsorption and dissociation over a pair of ZCu ions are associated with high barriers rendering also this structure improbable for H<sub>2</sub> consumption at experimental conditions. Thus, these structures are not included in the simulations of the H<sub>2</sub>-TPR profiles. For the remaining species, we simulate H<sub>2</sub>-TPR profiles based on the DFT energy landscapes (Figure 5), treating each Cu species separately. The reactions, including the kinetic parameters, are reported in Table S1.



**Figure 5.** Simulated H<sub>2</sub> consumption profile during TPR for  $Z_2CuOCu$ , ZCuOH,  $Z_2CuHOOHCu$ , paired  $Z_2Cu$ ,  $[Cu_2(NH_3)_4O_2]^{2+}$ ,  $Z_2CuOOCu$ , and isolated  $Z_2Cu$ . The dashed line indicates that  $[Cu_2(NH_3)_4O_2]^{2+}$  decomposes below the simulated consumption peak. Only one site is considered for each simulation. The heating rate and H<sub>2</sub> pressure are set to 10 °C/min and 2000 ppm, respectively.

 $Z_2CuOCu$  consumes  $H_2$  already at low temperatures with a maximum at 95 °C. ZCuOH has a peak at 150 °C.  $Z_2CuHOOHCu$  consumes  $H_2$  at 300 °C. Paired  $Z_2Cu$  consumes  $H_2$  at 420 °C, whereas isolated  $Z_2Cu$  does not consume  $H_2$  as this reaction is endothermic.  $[Cu_2(NH_3)_4O_2]^{2+}$  consumes  $H_2$  at 460 °C forming a broad peak. It should be noted that 460 °C is above the temperature for desorption of the NH<sub>3</sub> ligands. Thus,  $H_2$  consumption over  $[Cu_2(NH_3)_4O_2]^{2+}$  should experimentally be limited to the low-temperature tail.  $H_2$  adsorption on  $Z_2CuOOCu$  results in a broad peak at 520 °C.

To summarize, only the Cu species in oxidation state +2 consume H<sub>2</sub>. From the simulated H<sub>2</sub>-TPR profiles, the Cu species can be divided into three groups. The species that consume H<sub>2</sub> at low temperatures contain a single oxygen atom (Z<sub>2</sub>CuOCu and ZCuOH). Hydrogen can be adsorbed at Z<sub>2</sub>CuHOOHCu and paired Z<sub>2</sub>Cu species at medium temperatures. Species that consume H<sub>2</sub> at high temperatures contain two oxygen atoms ([Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup> and Z<sub>2</sub>CuOCu). **Measured H<sub>2</sub>-TPR Profiles.** Results from the H<sub>2</sub>-TPR

**Measured H<sub>2</sub>-TPR Profiles.** Results from the H<sub>2</sub>-TPR experiments are reported in Figure 6a–f. The profiles correspond to different pretreatments as shown in Figure 1. Figure 6a shows the H<sub>2</sub> consumption over the mobile  $[Cu(NH_3)_2]^+$  complexes, which turns out to be negligible. A pair of  $[Cu(NH_3)_2]^+$  can adsorb O<sub>2</sub>, forming  $[Cu_2(NH_3)_4O_2]^{2+}$ . The  $[Cu_2(NH_3)_4O_2]^{2+}$  complex consumes H<sub>2</sub> with a peak at 350 °C (Figure 6b). It is important to note that  $[Cu(NH_3)_2]^+$  and  $[Cu_2(NH_3)_4O_2]^{2+}$  are stable only below ~300 °C; thus, desorption of NH<sub>3</sub> is observed during the TPR



**Figure 6.** Experimental  $H_2$  consumption profile during TPR for different pretreatments. The pretreatments for each experiment are shown in Figure 1. The amounts of consumed  $H_2$  are no consumption, 0.06, 0.06, 0.12, 0.18, and 0.14  $\mu$ mol/mg<sub>cat</sub> for panels a, b, c, d, e, and f, respectively.

experiments (see the Supporting Information), indicating that the complexes decompose. For  $[Cu_2(NH_3)_4O_2]^{2+}$ , the desorption of NH<sub>3</sub> occurs simultaneously with the H<sub>2</sub> consumption. Hence, the amount and temperature at which  $[Cu_2(NH_3)_4O_2]^{2+}$  adsorbs  $H_2$  cannot be resolved unambiguously. H<sub>2</sub> consumption over a sample with dominantly ZCu has a peak at 490 °C as shown in Figure 6c. The frameworkbound dimer Z<sub>2</sub>CuOOCu (Figure 6d) has a broad peak starting at ~200 °C with a maximum at 490 °C. The temperature for the main peak is similar to ZCu. The profiles in Figures 6e and 6f are obtained over samples that have been pretreated with SCR conditions (Figure 6e) and SCR conditions followed by a dehydration step (Figure 6f). Figure 6e displays two peaks; a low-temperature peak at 230 °C and a high-temperature peak at 490 °C, possibly with a shoulder at 375 °C. After dehydration (Figure 6e), the low-temperature peak is removed, whereas the higher temperature peak and shoulder are unaffected.

#### DISCUSSION

In the literature, the measured H<sub>2</sub>-TPR profiles of Cu-CHA consist generally of three main peaks at 220, 360, and 500  $^{\circ}$ C.<sup>2-4,6,10-12</sup> Our measurement for H<sub>2</sub> consumption over a sample that is pretreated with SCR conditions shows similar low- and high-temperature peaks. The low-temperature peak in

The combination of a first-principles-based microkinetic model with H<sub>2</sub>-TPR measurements on samples with different pretreatments makes it possible to connect the consumption of H<sub>2</sub> with specific Cu species in the Cu-CHA samples. In the first-principles-based microkinetic modeling, we have considered a range of different Cu species. At low temperatures,  $Z_2$ CuOCu has a peak in the H<sub>2</sub> consumption at 95 °C and ZCuOH has a peak at 150 °C.  $Z_2$ CuHOOHCu and paired  $Z_2$ Cu species consume H<sub>2</sub> at 300 and 420 °C, respectively, and at high temperatures,  $[Cu_2(NH_3)_4O_2]^{2+}$  and  $Z_2$ CuOOCu show H<sub>2</sub> consumption at around 500 °C. We find that Cu ions in oxidation state +1 do not consume H<sub>2</sub>.

Experimentally, samples prepared with dominantly [Cu- $(NH_3)_2$ ]<sup>+</sup> do not show any H<sub>2</sub> consumption, in agreement with the simulations. The sample with [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup> shows some H<sub>2</sub> uptake. However, the peak at ~350 °C is above the NH<sub>3</sub> desorption temperature. Thus, the TPR profile should mainly originate from framework-bound Cu species, such as ZCu, ZCuNH<sub>3</sub>, or oxidized framework bound complexes, Cu<sub>x</sub>O<sub>y</sub>. The simulated profile of [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup> shows a peak at 460 °C. However, our simulations do not include the decomposition of [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup> above ~300 °C, and contributions to the H<sub>2</sub> consumption from [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup> should therefore only be expected from the tail at low temperatures.

The measurements of a sample with dominantly ZCu show a peak at 490 °C. This is in disagreement with the DFT calculations and could be related to the presence of paired  $Z_2Cu$  species also in this sample and/or some oxidation. The temperature at which  $H_2$  is consumed in Figure 6c is similar the temperature of the peak in Figure 6d, where  $Z_2CuOOCu$  was selectively prepared. In the literature,<sup>3,51</sup> ZCu has been assigned to a peak at very high temperatures (>800 °C). As this is in a temperature region where the CHA structure starts to degrade,<sup>4</sup> the  $H_2$  consumption could be connected to the formation of defects in the zeolite framework. Oxidized framework bound Cu shows a peak at 490 °C, which is in fair agreement with the simulated peak at 520 °C.

The sample that has been pretreated in SCR conditions (Figure 6e) shows two peaks at 230 and 490 °C, respectively. The low-temperature peak is close to the simulated peak for  $H_2$ consumption over ZCuOH, and assigning the low-temperature peak to ZCuOH agrees with previous suggestions.<sup>2,3,6</sup> Our simulations suggest that the high-temperature peak could be assigned to Z<sub>2</sub>CuOOCu. The simulated profile for the peroxo species [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup> has a peak at 460 °C. However, as already discussed, this temperature is higher than the desorption temperature of NH<sub>3</sub>, which means that the  $[Cu_2(NH_3)_4O_2]^{2+}$  species do not contribute directly to the TPR profile. In the literature, the high-temperature peak has previously been assigned to Z<sub>2</sub>Cu. We find that isolated Z<sub>2</sub>Cu does not consume  $H_2$ , whereas paired  $Z_2Cu$  consume  $H_2$  with a peak at about 420 °C. The computed peak at 420 °C from paired Z<sub>2</sub>Cu agrees also reasonably well with a feature at 360  $^{\circ}\text{C}\text{,}$  which is commonly reported in the literature  $^{2,10}$  and is typically assigned to  $Z_2Cu$ .

The fact that only paired  $Z_2Cu$  sites consume  $H_2$ , whereas isolated  $Z_2Cu$  does not, suggests that the distribution of  $Z_2Cu$ sites in Cu-CHA plays an important role for the  $H_2$ consumption. How close the  $Z_2Cu$  species should be to allow for  $H_2$  consumption cannot be investigated using only one hexagonal unit cell of CHA. However, as both Cu ions are reduced simultaneously, the Cu ions should be close enough to allow for the electron transfer. An increased Cu loading with constant Si/Al ratio should result in a larger fraction of paired  $Z_2$ Cu species.  $H_2$ -TPR experiments on samples with an Si/Al ratio of 9 and different Cu loadings (0.8–3.99%), show an increased  $H_2$  consumption for the high-temperature peak with higher Cu loading,<sup>10</sup> which is consistent with our study.

There are alternative distributions of the Al ions for the Cu complexes reported in Figure 2. By changing the location of the Al ions, the reactivity toward  $H_2$  may change, resulting in a shift of the  $H_2$ -consumption peak. To test the sensitivity, the  $H_2$  dissociation is calculated for paired  $Z_2Cu$  and  $Z_2CuOOCu$  with different Al distributions. For  $Z_2Cu$ , the Al ions are placed in the six-membered ring, separated by one Si atom, and for  $Z_2CuOOCu$ , the Al ions are placed opposite each other in the eight-membered ring. The simulated  $H_2$ -TPR profiles show peaks shifted by 10 and 90 °C to higher temperatures for the alternative Al distribution for  $Z_2CuOOCu$ , respectively. Thus, the sensitivity of the TPR profiles on the Al distribution are in these cases not substantial (see the Supporting Information for reaction landscapes and simulated  $H_2$ -TPR profiles).

Some H<sub>2</sub>-TPR studies have reported an H<sub>2</sub>/Cu ratio close to or slightly below 0.5, indicating that one H atom reacts per Cu atom.<sup>2,12</sup> The effective H<sub>2</sub>/Cu ratio for the reactions over ZCuOH and Z<sub>2</sub>CuOOCu is 1, whereas it is 0.5 over Z<sub>2</sub>CuOCu, Z<sub>2</sub>Cu, and Z<sub>2</sub>CuHOOHCu. This suggests that Z<sub>2</sub>CuOCu, paired Z<sub>2</sub>Cu, and Z<sub>2</sub>CuHOOHCu dominate the experimental samples. It should be stressed that the analysis of the H<sub>2</sub>/Cu is based on the assumption that all Cu ions in the sample are reduced, which may not be valid for samples with a distribution of Cu species.

#### CONCLUSIONS

We have used density functional theory to study the reaction of H<sub>2</sub> with selected Cu sites in Cu-CHA. The energy landscapes have been used as input to microkinetic modeling of H<sub>2</sub>-TPR profiles. In addition, we have measured H<sub>2</sub>-TPR profiles from samples that have been selectively prepared to contain dominant Cu species. The comparison between simulated and measured H<sub>2</sub>-TPR profiles allows us to identify and link the peaks in the H<sub>2</sub>-TPR profiles with certain Cu species. In the simulations we find that H<sub>2</sub> consumption over Cu species that in the +2 oxidation states ( $Z_2CuOCu$ , ZCuOH,  $Z_2Cu$ ,  $[Cu_2(NH_3)_4O_2]^{2+}$ , Z<sub>2</sub>CuHOOHCu, and Z<sub>2</sub>CuOOCu) From typical  $H_2$ -TPR profiles reported in the literature, we assign the low-temperature peak at 220 °C to ZCuOH, the mediumtemperature peak at 360 °C to Z<sub>2</sub>CuHOOHCu and paired Z<sub>2</sub>Cu species, and the high-temperature peak at 500 °C to paired Z<sub>2</sub>Cu species and Z<sub>2</sub>CuOOCu. Our study demonstrates the possibility to use DFT in combination with microkinetic modeling to interpret H2-TPR measurements, which enables linking the presence of certain Cu species with catalyst function.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.3c07998.

Additional settings for the microkinetic model and constrained molecular dynamic simulations together

with energy landscapes and measured  $NH_3$  desorption profiles (PDF)

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#### Notes

The authors declare no competing financial interest.

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