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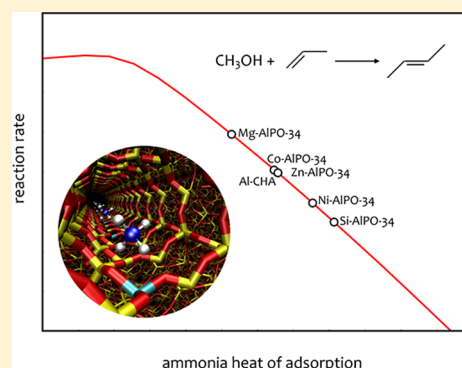
## Reactivity Descriptor in Solid Acid Catalysis: Predicting Turnover Frequencies for Propene Methylation in Zeotypes

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## S Supporting Information

**ABSTRACT:** Recent work has reported the discovery of metal surface catalysts by employing a descriptor-based approach, establishing a correlation between a few well-defined properties of a material and its catalytic activity. This theoretical work aims for a similar approach in solid acid catalysis, focusing on the reaction between propene and methanol catalyzed by Brønsted acidic zeotype catalysts. Experimentally, the ammonia heat of adsorption is often used as a measure of the strength of acid sites. Using periodic DFT calculations, we show that this measure can be used to establish scaling relations for the energy of intermediates and transition states, effectively describing the reactivity of the acid site. This allows us to use microkinetic modeling to predict a quantitative relation between the ammonia heat of adsorption and the rate of propene methylation from first principles. We propose that this is the first step toward descriptor-based design of solid acid catalysts.

**SECTION:** Surfaces, Interfaces, Porous Materials, and Catalysis



Modern society faces an urgent need for new catalysts to be used in processes for sustainable production of fuels and chemicals.<sup>1,2</sup> In the search for improved catalyst materials, it is essential to uncover the properties that determine the activity and selectivity of a given catalyst for a given reaction, the catalyst genome.<sup>3</sup> Considerable progress has been made in transition-metal catalysis by establishing a descriptor-based approach that allows correlating surface properties such as adsorption energies with the activity and selectivity of catalysts.<sup>4–7</sup> First examples have now emerged, where this descriptor-based approach enabled the discovery of new transition-metal-based catalysts.<sup>4–7</sup> This approach is still in its infancy in solid acid catalysis, and the theoretical work presented here aims at bringing it one step further, focusing exclusively on Brønsted acid catalysts. Whereas it seems obvious that the activity of a solid acid catalyst is related to its acidity, it is not always trivial to quantify this relation and identify a suitable descriptor. Experimentally, the strength of acid sites in solids is often quantified through the adsorption enthalpy of bases, such as ammonia or organic amines.<sup>8,9</sup> The deprotonation energy (DPE) provides an independent measure of intrinsic acid strength<sup>10</sup> and has been used in elegant studies of how acid strength influences single reaction steps.<sup>11–16</sup> It has been pointed out that as opposed to DPE, the ammonia

adsorption enthalpy  $\Delta H_{\text{ads}}(\text{NH}_3)$  is not a rigorous measure of intrinsic acid strength as it contains contributions from the interaction between the ammonium ion and the deprotonated acid site.<sup>10</sup> On the other hand, this makes  $\Delta H_{\text{ads}}(\text{NH}_3)$  interesting as a descriptor of the activity of solid acid catalysts as it captures how the catalyst interacts with the reactants. Hence,  $\Delta H_{\text{ads}}(\text{NH}_3)$  can be thought of as a measure of the reactivity of a given site, and we will show here how it correlates to catalytic activity.

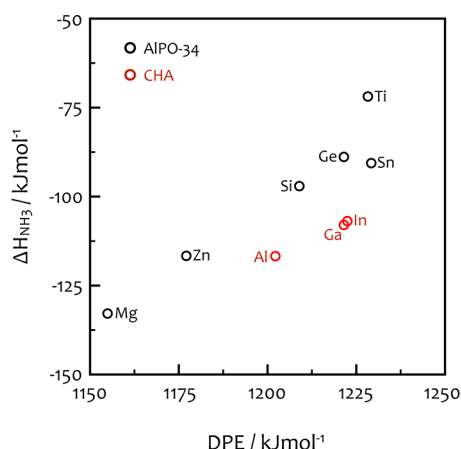
Zeolites, or more generally zeotype materials, are among the most widely used solid acid catalysts in industry, in particular, in fluid catalytic cracking, hydrocracking, alkylation, and methanol-to-hydrocarbon (MTH) reactions.<sup>17–21</sup> Zeotype materials are also particularly interesting solid acids for fundamental investigations as their highly regular crystalline structures ensure well-defined acid sites. We have chosen the reaction between methanol and propene to yield butene, a central part of the MTH process,<sup>22</sup> to show how a descriptor-based approach can be established in solid acid catalysis. As model catalysts, we employ zeotype materials possessing the CHA

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framework topology,<sup>23</sup> that is, substituted microporous aluminosilicates and aluminophosphates (Figure S1, Supporting Information (SI)). These solids contain one type of acid site, the strength of which is changed by isomorphic substitution of metal atoms in the framework. We choose the following naming convention: substituted zeolites are named Me-CHA, where Me indicates an isomorphically substituted metal. In this nomenclature, Al-CHA is the common zeolite H-SSZ-13.<sup>24,25</sup> Analogously, metal-substituted aluminophosphates are named Me-AlPO-34, such that Si-AlPO-34 is the well-known H-SAPO-34 material.<sup>24,25</sup> Density functional theory (DFT) is used to calculate reaction energy profiles for a variety of substituted zeotype materials and correlate the energies with the acid site reactivity as measured by  $\Delta H_{\text{ads}}(\text{NH}_3)$ . Finally, we construct a microkinetic model that allows us to correlate the catalytic activity with this reactivity, placing zeolites and zeotypes on the same footing.

We start out by addressing the issue of measuring the acidity of solid Brønsted acids. We have calculated  $\Delta H_{\text{ads}}(\text{NH}_3)$  in Al-CHA to  $-118$  kJ/mol, which is in reasonable agreement with the experimental result of  $-131$  kJ/mol.<sup>26</sup> In addition to ammonia adsorption and DPE, the acid strength is often quantified by adsorbing CO on the sites and measuring the shift of the O–H stretching frequency in the infrared spectrum.<sup>9,27</sup> This shift has been measured for Al-CHA ( $314\text{ cm}^{-1}$ ) and Si-AlPO-34 ( $274\text{ cm}^{-1}$ ).<sup>28</sup> Our calculations perfectly reproduce the shift in Al-CHA ( $319\text{ cm}^{-1}$ ), while the agreement is fair for Si-AlPO-34 ( $247\text{ cm}^{-1}$ ). The latter discrepancy can be explained by formation of Si islands in Si-AlPO-34,<sup>29</sup> leading to acid sites most probably more similar to those in Al-CHA than the truly isolated sites considered here. We conclude that our computational setup is capable of describing the interactions between molecular species and acid sites in zeotype materials. We now turn to discuss DPE and  $\Delta H_{\text{ads}}(\text{NH}_3)$  to lead in to our argument that the latter is a good descriptor of the reactivity of an acid site. Figure 1 shows



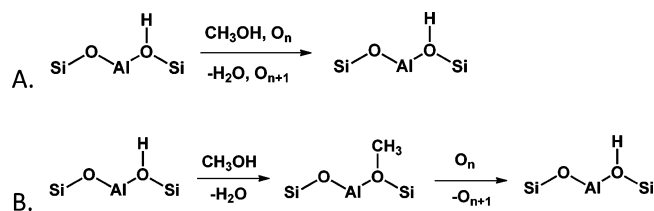
**Figure 1.** The relation between  $\Delta H_{\text{ads}}(\text{NH}_3)$  and DPEs for a series of metal-substituted AlPO-34 and CHA acid catalysts. DPEs have been calculated using a cluster model (see the SI).

the relation between  $\Delta H_{\text{ads}}(\text{NH}_3)$  and the intrinsic acid strength measured by DPE, calculated for a number of acidic zeotype materials where a metal substitution generates one Brønsted acid site per unit cell.

While as a rough trend ammonium binds stronger with decreasing DPE, the correlation is rather poor, as pointed out

in previous work.<sup>10</sup> The deviations can be attributed mainly to two effects. First, the catalyst framework also contributes to  $\Delta H_{\text{ads}}(\text{NH}_3)$ . In other words, acid sites of the same intrinsic acid strength (DPE) can show different  $\Delta H_{\text{ads}}(\text{NH}_3)$ , depending on the chemical composition of the framework surrounding the acid site. The second reason for the deviations is that  $d\Delta H_{\text{ads}}(\text{NH}_3)/d\text{DPE}$  decreases with DPE. This is due to ion pair interaction; as the acid strength increases (DPE decreases), the negative charge of the corresponding base becomes more delocalized. This reduces the interaction with the localized charge of the ammonium ion<sup>10,13</sup> and thereby  $d\Delta H_{\text{ads}}(\text{NH}_3)/d\text{DPE}$ . Hence,  $\Delta H_{\text{ads}}(\text{NH}_3)$  does not provide a rigorous measure of the intrinsic acid strength of solid acids. Importantly, however, it captures the interactions determining the stability of positively charged intermediates and transition states. We therefore propose that  $\Delta H_{\text{ads}}(\text{NH}_3)$  is a good descriptor of the reactivity of an acid site. We will substantiate this in the following, using the methanol–propene reaction as an example. Scheme 1 shows the reaction pathways commonly assumed in zeolite-catalyzed methanol–alkene reactions.<sup>30</sup>

**Scheme 1.** Pathways of the Zeolite-Catalyzed Reaction between Methanol and Alkenes ( $\text{O}_n$ ) to Form Longer Alkenes ( $\text{O}_{n+1}$ )<sup>a</sup>

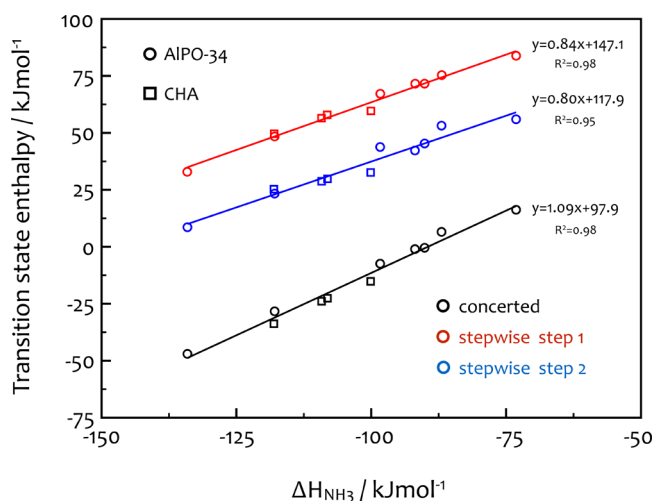


<sup>a</sup>(A) Concerted; (B) stepwise.

We have recently shown that the stepwise pathway prevails in zeolite H-ZSM-22 at conditions applied in common experiments on MTH conversion.<sup>31</sup> As the preferred pathway might change with acid strength and framework, however, we considered both routes in this work. We have located all intermediates and transition states for a series of substituted zeotype materials using periodic DFT calculations. The calculations employ the BEEF-vdW functional<sup>32</sup> that has been shown to accurately model dispersion forces and methylation reactions in zeolites.<sup>31,33,34</sup>

Figure 2 shows the enthalpies of the three transition states as a function of  $\Delta H_{\text{ads}}(\text{NH}_3)$ . The observed correlations are remarkably good, showing that  $\Delta H_{\text{ads}}(\text{NH}_3)$  captures the interactions between the positively charged transition states and the deprotonated acid site in the catalysts. In other words,  $\Delta H_{\text{ads}}(\text{NH}_3)$  measures the reactivity of an acid site in terms of its ability to transfer a proton and stabilize the resulting charged species. Importantly, the descriptor includes the influence of the framework; both zeolites and aluminophosphate materials fall on the same scaling line. Note that the correlation between the transition-state enthalpies and the DPE values is much less pronounced (Figure S6, SI).

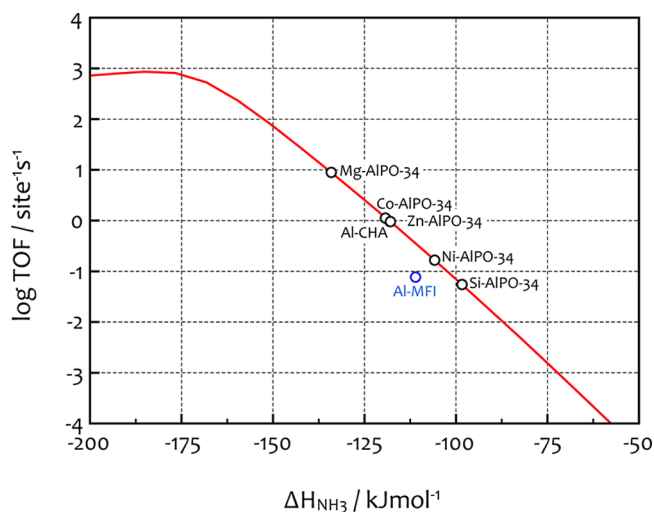
While the transition-state enthalpies are highly dependent on the acid site reactivity, the neutral alkoxy intermediates exhibit slopes close to zero when correlated with  $\Delta H_{\text{ads}}(\text{NH}_3)$  (Figure S5, SI). These intermediates are rather insensitive to the reactivity of the acid site because they are bound covalently;<sup>35</sup> the homolytic dissociation energy of the C–O bond is largely independent of the ionic interactions determining  $\Delta H_{\text{ads}}(\text{NH}_3)$ .



**Figure 2.** Linear scaling relations between the transition-state enthalpies (referenced to the gas-phase reactants) and  $\Delta H_{\text{ads}}(\text{NH}_3)$  for methanol-propene reaction through the concerted and stepwise pathways.

On the other hand, charged intermediates like protonated methanol and 2-butylium exhibit scaling lines with slopes close to 1 (Figure S5, SI). It follows that for sufficiently reactive acid sites, the ion pair can become more stable than the neutral species. Interestingly,  $\Delta H_{\text{ads}}(\text{NH}_3)$  functions as a descriptor for different transition states and intermediates, making the correlation different from Brønsted-Evans-Polanyi relationships, where a single barrier is correlated with a reaction energy.<sup>36</sup>

Having established scaling relations for intermediates and transition states, we employed a microkinetic model of the methanol-propene reaction, including both methylation pathways, allowing us to calculate turnover frequencies (TOFs) as a function of  $\Delta H_{\text{ads}}(\text{NH}_3)$ . The outcome of this model can be seen in Figure 3. Our predictions are in good agreement with

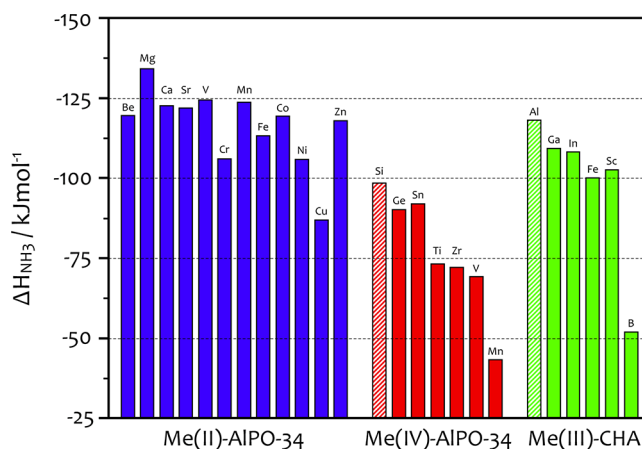


**Figure 3.** The relation between calculated  $\Delta H_{\text{ads}}(\text{NH}_3)$  and the simulated TOF (see reaction conditions in the Computational Details section) for the methanol-propene reaction catalyzed by Me-CHA and Me-AlPO-34 materials. The calculated  $\Delta H_{\text{ads}}(\text{NH}_3)$  values of selected catalysts are highlighted. The Al-MFI point represents the TOF extracted from the experiments of Svelle et al.<sup>37</sup>

results from kinetics experiments in Al-MFI (H-ZSM-5).<sup>37</sup> We take this agreement as a rough validation of the absolute values of the predicted TOFs, keeping in mind that Al-MFI contains several different sites of which some might be inaccessible to propene methylation.

Generally, more reactive acid sites lead to more active catalysts; the TOF increases by roughly an order of magnitude for every 20 kJ/mol decrease in  $\Delta H_{\text{ads}}(\text{NH}_3)$  for the zeotypes investigated here. However, for highly reactive sites, the situation changes; when (charged) intermediates bind too strongly to the catalyst, they will poison the active sites and decrease the catalytic activity. As Figure 3 illustrates, the model predicts the activity to reach a maximum at  $\Delta H_{\text{ads}}(\text{NH}_3) = -175 \text{ kJ/mol}$  for the methylation of propene. Here, protonated methanol binds strongly to the acid site (Figure S8, SI). While that reactive acid sites are likely inaccessible in zeotype materials, we note that the optimal reactivity can shift considerably with the reaction considered. In general, the optimal acid-site reactivity decreases with decreasing temperature, as the entropy loss of adsorption decreases and adsorbates bind stronger.

In order to investigate the extent to which isomorphic substitution of zeotypes influences the reactivity and hence activity of the acid sites, we calculated  $\Delta H_{\text{ads}}(\text{NH}_3)$  for a range of metal substitutions in the zeolite and zeotype materials, as indicated in Figure 4. As the materials considered here span 75



**Figure 4.** Calculated adsorption enthalpies of ammonia in metal-substituted AlPO-34 and CHA solid acid catalysts.

kJ/mol in  $\Delta H_{\text{ads}}(\text{NH}_3)$ , we obtain an increase in the TOF of propene methylation of more than 5 orders of magnitude between the least and most active acid catalysts (cf. Figure 3). To generate an acid site in the CHA zeolite by isomorphic substitution, the only possibility is to substitute  $\text{Si}^{\text{IV}}$  with a  $\text{Me}^{\text{III}}$ . Al-CHA possesses the most reactive acid sites of these zeolites, whereas the common Si-AlPO-34 is a significantly less reactive acid. However, due to the larger variety of substitutions ( $\text{Al}^{\text{III}}$  with  $\text{Me}^{\text{II}}$  or  $\text{P}^{\text{V}}$  with  $\text{Me}^{\text{IV}}$ ), it is possible to tune the reactivity of acid sites in AlPO-34 considerably more than in CHA. We find that  $\text{Mg}^{\text{II}}$  substitution leads to the most reactive acid with an  $\Delta H_{\text{ads}}(\text{NH}_3)$  of  $-134 \text{ kJ/mol}$ . We therefore propose that Mg-AlPO-34 is the most active catalyst for the methylation of propene identified in this study. Judging from Figure 4, it seems that this is indeed the highest reactivity that can be obtained by isomorphic substitution. Other solid acids



like Keggin polyoxometalates, however, are known to exhibit acid strengths superior to those of zeotype materials.<sup>12</sup>

At this point, it is appropriate to consider the scope of applications of the methodology presented here. Interestingly, the model predicts Al-CHA to be more active than Si-AlPO-34 in propene methylation (Figure 3), which mirrors the experimental observation that Al-CHA is more active than Si-AlPO-34 in methanol-to-olefins (MTO) conversion.<sup>37</sup> In addition, the calculated  $\Delta H_{\text{ads}}(\text{NH}_3)$  describes the trend observed in MTO conversion (Figure S7, SI) on isomorphically substituted AlPO-18 catalysts (with the AEI framework topology,<sup>23</sup> which has virtually the same cavity size as the CHA topology).<sup>38</sup> Collectively, these observations suggest that the (calculated) heat of adsorption of ammonia as an activity descriptor can be extended to MTO conversion, the framework topology and reaction conditions being equal. In this respect, it is important to point out that in the methodology presented here, the acid sites are isolated in the sense that each molecular species interact with only one acid site at a time. It is hence unclear if the methodology is applicable to zeolites or zeotypes with a high density of acid sites, where molecular species can interact with more than one acid site at a time.

Whereas the present work considered zeotype materials, we speculate that  $\Delta H_{\text{ads}}(\text{NH}_3)$  could be a general reactivity descriptor of solid acids with sites of greater or similar strength. We base this on the following reasoning; the interactions between the molecular species and the zeolite framework clearly depend on the species and are not captured by  $\Delta H_{\text{ads}}(\text{NH}_3)$ . They are, however, independent of acid-site strength (and reactivity) and hence captured in the intercept of the scaling lines. We therefore suggest that similar scaling lines exist for Brønsted acid sites in other materials, each with a characteristic value of the intercept for each species. For acid sites of lower strength than the ones studied here, the negative charge of the deprotonated site is highly localized, presumably making hydrogen bonding a major contributor to  $\Delta H_{\text{ads}}(\text{NH}_3)$ . This would limit the applicability of  $\Delta H_{\text{ads}}(\text{NH}_3)$  as an activity descriptor for weak acid catalysts. Finally, it has to be stressed that  $\Delta H_{\text{ads}}(\text{NH}_3)$  is intended to capture the reactivity of an acid site within a material and cannot give information about its accessibility or the shape selectivity of the catalyst. Information about the former could in principle, however, be obtained by considering larger bases, as often done experimentally.<sup>27,39</sup>

To summarize, we have investigated the methanol–propene reaction central to methanol-to-olefins conversion catalyzed by acidic zeolites and zeotypes. It was possible to correlate the enthalpies of all transition states and intermediates with the acid site reactivity of the catalysts, as quantified by  $\Delta H_{\text{ads}}(\text{NH}_3)$ , placing zeolites and zeotypes on the same footing. These correlations were employed in a microkinetic model, allowing us to obtain a quantitative relation between the TOF and  $\Delta H_{\text{ads}}(\text{NH}_3)$  for the acid catalysts. This shows that catalytic activity in propene methylation is predominantly controlled by stabilization of species with a rather localized positive charge, as captured by  $\Delta H_{\text{ads}}(\text{NH}_3)$ . When applied to other reactions involving electronically conjugated species, probe molecules with a more delocalized charge might be better suited than ammonia. The methodology, however, is equivalent and can provide quantitative correlations between catalytic activity and the reactivity of acid sites, enabling prediction of the optimal solid acid catalyst for a given reaction. This approach opens an exciting new avenue for understanding and designing solid acid catalysts guided by first-principles

calculations using descriptors that are accessible experimentally as well as computationally.

## ■ COMPUTATIONAL DETAILS

All DFT calculations were performed with the GPAW package, a real-space grid implementation of the projector augmented wave method.<sup>40</sup> The calculations employed the Bayesian error estimation functional with van der Waals correlation (BEEF-vdW).<sup>32</sup> The CHA and AlPO-34 frameworks were represented by periodic 36T hexagonal cells. Lattice constants were optimized to  $a = b = 13.90$  Å and  $c = 15.11$  Å for AlPO-34 and  $a = b = 13.80$  Å and  $c = 14.84$  Å for CHA. The AEI and AlPO-18 frameworks were represented by periodic 48T cells. Lattice constants were optimized to  $a = 13.82$  Å,  $b = 12.66$  Å, and  $c = 18.61$  Å for AEI and  $a = 13.83$  Å,  $b = 12.73$  Å, and  $c = 18.72$  Å for AlPO-18. Substitution of Si (CHA), P, or Al (AlPO-34) with a metal atom generated one Brønsted acid site per unit cell, having the proton in the O2 position.<sup>41</sup> Unless otherwise indicated, the materials employed were Si-, Ge-, Sn-, Ti-, Mg-, Zn-, and Cu-AlPO-34 as well as Al-, Ga-, In-, and Fe-CHA. Analogous substitution was performed in AlPO-18 to arrive at the T2O2 Brønsted site.<sup>23</sup> Cluster calculations on the CHA and AlPO-34 frameworks were performed with non-periodic boundary conditions on 48T clusters terminated by H atoms with fixed positions. The DPEs were calculated as

$$\text{DPE} = E(\text{A}^-) + E(\text{H}^+) - E(\text{AH})$$

from electronic energies of the relaxed structures of the protonated (AH) and deprotonated ( $\text{A}^-$ ) cluster species as well as the isolated proton. Ammonia adsorption in Al-MFI was calculated at the T12-O24 site, employing the computational setup described previously.<sup>33</sup> The free energies of all species were calculated from harmonic frequencies. Calculated enthalpies are stated at 0 K as the correction from heat capacity is generally within 5 kJ/mol for temperatures up to 623 K (Table S2, SI). The microkinetic model was solved using CatMAP,<sup>42</sup> employing a steady-state solution of the rate equations. The model used a temperature of 623 K and partial pressures of methanol, propene, water, and 2-butene of 0.35, 0.35, 0.15, and 0.15 bar, respectively. Further details can be found in the SI.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Structures of the periodic and cluster models; additional details on the DFT and thermochemistry calculations; additional results from comparison of periodic and cluster models; calculated OH frequency shifts by CO adsorption on Me-CHA and Me-AlPO-34 materials; calculated heats of ammonia adsorption and experimentally measured MTO conversion in Me-AlPO-18 materials; scaling relations for reaction intermediates with  $\Delta H_{\text{ads}}(\text{NH}_3)$  and transition states with DPE; and technical details and input for the microkinetic modeling. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Author Contributions

<sup>‡</sup>C.-M.W. and R.Y.B. contributed equally to this work.

## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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