Scaling relations for acidity and reactivity of zeolites

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Scaling Relations for Acidity and Reactivity of Zeolites
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ABSTRACT: Zeolites are widely applied as solid acid catalysts in various technological processes. In this work we have computationally investigated how catalytic reactivity scales with acidity for a range of zeolites with different topologies and chemical compositions. We found that straightforward correlations are limited to zeolites with the same topology. The adsorption energies of bases such as carbon monoxide (CO), acetonitrile (CH3CN), ammonia (NH3), trimethylamine (N(CH3)3), and pyridine (C5H5N) give the same trend of acid strength for FAU zeolites with varying composition. Crystal orbital Hamilton populations (COHP) analysis provides a detailed molecular orbital picture of adsorbed base molecules on the Bronsted acid sites (BAS). Bonding is dominated by strong σ donation from guest molecules to the BAS for the adsorbed CO and CH3CN complexes. An electronic descriptor of acid strength is constructed based on the bond order calculations, which is an intrinsic parameter rather than adsorption energy that contains additional contributions due to secondary effects such as van der Waals interactions with the zeolite walls. The bond order parameter derived for the CH3CN adsorption complex represents a useful descriptor for the intrinsic acid strength of FAU zeolites. For FAU zeolites the activation energy for the conversion of π-adsorbed isobutene into alkoxy species correlates well with the acid strength determined by the NH3 adsorption energies. Other zeolites such as MFI and CHA do not follow the scaling relations obtained for FAU; we ascribe this to the different van der Waals interactions and steric effects induced by zeolite framework topology.

1. INTRODUCTION
Zeolites are well-defined microporous crystalline solids widely applied in various technological processes.1 The crystalline architecture of these materials is built of SiO4 and AlO4 tetrahedra linked by corner-sharing O atoms resulting in three-dimensional frameworks containing channels and cavities of molecular dimensions. The presence of tetrahedral Al3+ sites in the lattice gives rise to localized framework negative charge that is balanced by extraframework cations. The compensation in the lattice gives rise to localized framework negative charge σ-

Upon adsorption these bases react with the zeolite Bronsted acid sites (BAS) and the acid strength is correlated either directly to the heat of adsorption measured by calorimetry or temperature-programmed desorption or indirectly to the degree of perturbation of the adsorbed molecules, which can be monitored by spectroscopy (e.g., Fourier transform infrared (FTIR), NMR).

Despite a general consensus that acidity is key to the catalytic properties of zeolites, it has been difficult to ascertain quantitative structure-reactivity relations.7 Unlike homogeneous Brønsted acids, whose properties can be directly related to intrinsic acidity via pKa values, the acid activity of solids also depends on secondary effects related to the specific structural and topological properties. Furthermore, the substantial heterogeneity of acid sites due to the presence of defects and other structural inhomogeneities of practical zeolite catalysts additionally complicates establishing structure-performance relations solely from experimental data.10 Over the past decade, the development of scaling relations represents an important

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advance in the field of theoretical heterogeneous catalysis.\textsuperscript{11−14} These scaling relations rely on correlations between adsorption properties of chemical intermediates across different catalyst surfaces. Together with the Bronsted–Evans–Polanyi relationships,\textsuperscript{15,16} which link activation barriers to thermochemical reaction energies, it allows description of the catalytic activity in terms of descriptors such as adsorption energies of reaction intermediates. Despite the widespread use of the descriptor-based method in metal (oxide) surface catalysis, its application in zeolite catalysis has been limited so far.\textsuperscript{17−19}

The intrinsic strength of the BAS in zeolites can be determined by the deprotonation energy (DPE), which is the energy required to dissociate the Bronsted proton to an infinite distance.\textsuperscript{20−25} Iglesia et al.\textsuperscript{23−29} demonstrated a good correlation between the DPE values and the turnover rates and rate constants of catalytic reactions such as alcohol dehydration and skeletal isomerization of alkenes on zeolites and Keggin polyoxometalate (POM) clusters. Niwa and co-workers\textsuperscript{30} also found that the apparent activation barrier of alkane cracking strongly correlates with the DPE for a series of HY and cation-exchanged HY zeolites. However, more recent studies suggest that the DPE is an incomplete descriptor to capture the catalytic activity of solid acids, because other factors such as the interaction of the cationic transition state with the conjugate anionic zeolite framework also affect catalyst reactivity.\textsuperscript{18,31,32} An alternative acidity descriptor for zeolites is the adsorption heat of bases. The theoretical work by Borges et al.\textsuperscript{33} showed that a linear relationship exists between the adsorption enthalpy of ammonia and the activation energy for the protolytic cracking of \textit{n}-hexane in H–ZSM zeolites. This is consistent with the experimentally observed correlation between the turnover frequency and the activation energy of catalytic alkane cracking with the zeolite acidity measured by the heat of ammonia adsorption.\textsuperscript{34} Studt et al.\textsuperscript{17,18} also employed the heat of ammonia adsorption as a reactivity descriptor for the activity of chabazite zeolite and zeotype (silicoaluminophosphate) acid catalysts toward methanol–alkene reactions. They showed that the heat of ammonia adsorption can be used as a good descriptor for the energy of intermediates and transition states as well as the rate of alkene methylation predicted from microkinetic modeling. On the other hand, no general scaling relations were observed among different zeolite topologies (CHA, AEI, and AFI).\textsuperscript{19}

In this work we employed periodic density functional theory (DFT) calculations to investigate in detail the interaction of acidic sites in zeolite with common basic molecular probes and with alkenes to explore scaling relations between zeolite acidity and catalytic reactivity. To this end, we analyzed the effect of the variation of the zeolite chemical composition and topological properties (Figure 1) on the computed acid properties. FAU models were constructed with varying density of Al substitution (Si/Al ratio), different substituted heteroatom-containing models [FAU-Fe (Si/Fe = 47) and FAU-Ga (Si/Ga = 47)], silicoaluminophosphate SAPO-37 [FAU-Fe (Si:P:Al = 1:23:24)], extraframework-cation-containing models [FAU-EFAI-mono (Si/Al\textsubscript{P} = 7 and Si/Al\textsubscript{total} = 6), FAU-EFAI-bi (Si/Al\textsubscript{P} = 7 and Si/Al\textsubscript{total} = 4.7), and FAU-Na (Si/Al = 7)], and high-silica CHA (Si/Al = 35) and MFI (Si/Al = 95).
oatom (Fe and Ga zeolites), silicoaluminophosphate (SAPO) form, and the presence of extraframework cations. High silica CHA and MFI models were also investigated to account for the effect of pore size and zeolite topology. In the search for a fundamental acidity descriptor, crystal orbital Hamilton populations (COHP) analysis was employed to quantify the chemical interactions and bonding characteristics between the zeolite BAS and the adsorption probes. Alkene (isobutene and ethene) protonation was used as a model hydrocarbon activation process used to probe the catalytic reactivity of the zeolite models.

2. METHODS

2.1. DFT Calculations. Periodic DFT calculations were performed with VASP 5.3.5 using the Perdew–Burke–Ernzerhof (PBE) functional. The electron–ion interactions were described with the projected augmented waves (PAW) method. The Brillouin zone sampling was restricted to the Γ point. The energy cutoff was set to 500 eV. van der Waals interactions were described by the dispersion-corrected DFT-D2 method. Convergence was assumed to be reached when the force on each atom was below 0.03 eV Å⁻¹. A modest Gaussian smearing of 0.05 eV was applied to band occupations around the Fermi level, and the total energies were extrapolated to the reaction path obtained with the CI-NEB method. The maximum energy geometries along the reaction path obtained with the CI-NEB method were further optimized using a quasi-Newton algorithm.

2.2. Zeolite Models. Models with FAU topology were simulated by a rhombohedral unit cell (Si₄₈O₉₆). To construct Al-substituted FAU models with varied acidity, both lattice Al density and the presence of extraframework species were considered. Defect-free Al-FAU sites with different Si/Alₚ ratios of 47, 7, and 2.4 were constructed by introducing, respectively, 1, 6, and 14 Alₚ lattice substitutions per unit cell. Faujasite contains only one crystallographically distinct T site. Similar to our previous studies, the locations of framework Al were selected on the basis of the stability analysis. The Bronsted protons as charge-compensating cations were introduced at the O1 positions, which have been earlier identified as the preferred proton-acceptor sites. The cell parameters were optimized for the defect-free zeolite models. The optimized lattice parameters were as follows: FAU-47, a = b = c = 17.29 Å, α = β = γ = 60°; FAU-7, a = b = c = 17.44 Å, α = β = γ = 60°; FAU-2.4, a = b = c = 17.65 Å, α = β = γ = 60°. The increase of the unit cell dimensions with decreasing Si/Alₚ ratio is consistent with the experimental observations.

All FAU models containing extraframework cations were made from a unit cell with Si/Alₚ = 7. Three FAU models modified by EFAI species (Figure 1, FAU-EFAI-mono, FAU-EFAI-bi, and FAU-EFAI-tri) were considered, which contain mononuclear [AlOH]²⁺, binuclear [Al₂O₄H₄]²⁺, and trinuclear [Al₃O₆H₆]⁴⁺, respectively, as identified with high intrinsic stabilities in our previous studies. These cationic EFAI species were located in the faujasite sodalite cages with vicinal supercage BAS, and the induced positive charge by EFAI species was compensated by removing the protons to keep the system neutral. The Na-containing model (Figure 1, FAU-Na) was built by replacement of the trinuclear EFAI cluster with four Na cations located in the six-membered rings of the sodalite cage, facing the hexagonal prisms. Full geometry optimization with extraframework cations and guest molecules was performed with fixed cell parameters.

The iron- and gallium-substituted zeolite models (Figure 1, FAU-Fe and FAU-Ga) were obtained by isomorphous substitution of framework Al in FAU-47 model with trivalent Fe and Ga, and the lattice parameters were kept same as the optimized values of the FAU-47 model. In the case of the FAU-Fe model, spin-polarized calculations were carried out with high spin state (S = 5/2) identified as the most stable configuration. SAPO-37 (Figure 1, FAU-SAPO), which is the silicoaluminophosphate form of FAU, contains AlPO₄ units with isomorphous substitution of siliceous FAU framework, and one proton was introduced by substitution of P by Si in the unit cell. The optimized lattice parameters of FAU-FAU-SAPO are a = b = c = 17.48 Å, and α = β = γ = 60°.

The high silica CHA (Si/Al = 35) and MFI (Si/Al = 95) zeolite models (Figure 1, CHA and MFI) were represented by periodic 36T and 96T unit cells, respectively. Similar to the FAU-47 model, one lattice Si was replaced by an Al atom to introduce a BAS. Chabazite contains a single T site, and the Bronsted proton was placed on the O2 oxygen site, which represents one out of two highly populated acid sites. In the MFI model, an Al atom was introduced at the T12 crystallographic position at the channel intersection, and the charge-compensating proton was located on the O20 position following the thermodynamic considerations by Svelle et al.

2.3. Chemical-Bonding Analysis. Electronic structure analysis was performed with the LOBSTER 2.1.0 program. The partial density of states (PDOS) and crystal orbital Hamilton populations (COHP) were used to analyze chemical bonding of the systems. The PDOS plots provide information on the partial electron density distribution of a particular atomic orbital. The COHP densities give the electron density distribution of bonding and antibonding orbital fragments. Here the negative contributions of COHP (−COHP) were plotted, and the positive/negative peaks in the plots indicate the bonding/antibonding interaction regimes. All the figures were plotted with the Fermi level set as the reference point at 0 eV. The bond orders were computed by the density derived electrostatic and chemical (DDEC) method.

3. RESULTS AND DISCUSSION

3.1. Adsorption of Bases. The acid strength of zeolite models was probed by studying their adsorption complexes with base molecules of varying strength and size, namely, carbon monoxide (CO), acetonitrile (CH₃CN), ammonia (NH₃), trimethylamine (N(CH₃)₃), and pyridine (C₅H₅N). These molecular probes are commonly employed in experimental studies to assess acidities of solid catalysts. The strength of the bases can be accessed by their proton affinity, which is the negative of the enthalpy change in the reaction between the bases and proton to form the conjugate acids in the gas phase. According to the proton affinity, the strength of the base probes follows the trend CO (594 kJ/mol) < CH₃CN (779 kJ/mol) < NH₃ (854 kJ/mol) < N(CH₃)₃ (949 kJ/mol) < C₅H₅N (930 kJ/mol). Besides the base strength of the probes, the adsorption heats of these bases in microporous zeolites are also affected by the strength of the acid sites as well.
as the confinement effect due to different molecular sizes of the probes.

We have optimized the adsorption complexes in zeolites with one probe molecule per unit cell. Independent of the zeolite model, the adsorption complexes of a particular probe are structurally similar. Representative optimized structures of the adsorption complexes formed in the high-silica Al-substituted faujasite model (FAU-47) are shown in Figure 2. The interaction of CO and CH₃CN with BAS gives rise to molecular adsorption complexes, where the bonding is dominated by donor–acceptor-type interaction between the lone pairs of the adsorbed molecule and the acidic proton. On the contrary, the adsorption of much stronger NH₃, N(CH₃)₃, and C₅H₅N base results in the complete deprotonation of BAS to form contact ion-pair complexes confined in the zeolite cages.

DFT-computed adsorption energies (∆E_ads) are summarized in Table 1. ∆E_ads is the relative energy of the adsorption complex with respect to the free model and the probe in the gas phase (ΔE_ads = E_ads − E_model − E_probe). For the faujasite (FAU) models, the adsorption heats (∆ΔE_ads) increase in the sequence CO < CH₃CN < NH₃ < N(CH₃)₃ < C₅H₅N. The experimentally reported adsorption heat of CO on a faujasite-type H-Y zeolite (Si/Al = 5.6) is 26 kJ/mol,⁶⁵ which is close to our calculated value of 30 kJ/mol for FAU-7 model with a similar Si/Al ratio. Expectedly, due to its very low basicity, ∆E_ads(CO) does not vary significantly for the different FAU models, predicting that the CO molecular probe is not sufficiently sensitive to discriminate acidity variations. The differences in acidity of the models can be appreciated by more basic adsorption probes. Experimental studies reported adsorption heats of 110 kJ/mol for ammonia on a low-silica H-Y,⁶⁶ while the adsorption heats of 150 and 180 kJ/mol were reported for ammonia and pyridine, respectively, on a high-silica H-form of faujasite.⁶⁷ The computed adsorption energies for the current FAU models (Table 1) are in good agreement with these experimental values. The trend shows that the intrinsic acid strength gradually increases with decreasing Al density in the framework (increasing Si/Alₚ ratio). The acid strength of bridging OH groups is a function of the electronegativity of the T atoms both in the first coordination sphere and in the second coordination sphere of BAS. For Al-FAU, the decrease of Al concentration at next-nearest-neighbor (NNN) positions leads to increased acid strength. This effect manifests itself only at low-to-intermediate Si/Al ratios (typically Si/Al < 5).⁶⁸ For high dilution of framework Al (high Si/Al ratio), the NNN-Al effect vanishes and the acid strength levels off.⁶⁹ A more direct way to affect zeolite acidity is to vary the heteroatom substituting for Si in the framework. For the current models, the measured acid strength of the high-silica FAU models increases with decreasing electronegativity of the T atom: FAU-47 (χₐl = 1.61) > FAU-Ga (χₐl = 1.81) >
FAU-Fe ($\chi_{\text{Fe}} = 1.83$), in agreement with previous experimental and theoretical studies.\textsuperscript{10,65}

Aluminophosphates (AlPO₄) can be obtained in similar porous structures as aluminosilicate zeolites, in which a pair of Si⁴⁺ ions is substituted by Al³⁺ and P⁵⁺. Acidic silicoaluminophosphate (SAPO) zeotypes are obtained by substituting a fraction of P⁵⁺ by Si⁴⁺. Experimental studies\textsuperscript{66–70} report that SAPO-type zeolites usually display weaker acidity than their aluminosilicate counterparts (for example, SAPO-34 vs SSZ-13 materials with the CHA topology). Consistent with these experimental observations, the comparison of the ΔE_ads values of base probes (Table 1, FAU-SAPO vs FAU-47, ΔE_ads(CH3CN) = −83 vs −90 kJ/mol, ΔE_ads[NH3] = −120 vs −142 kJ/mol, ΔE_ads[N(CH3)3] = −174 vs −185 kJ/mol, and ΔE_ads[C6H5N] = −178 vs −192 kJ/mol) indicates weaker acid strength of BAS in FAU-SAPO than in FAU-47. The weaker acidity in SAPO was proposed to be due to the higher flexibility of the Al–O–P unit than the Si–O–Si unit.\textsuperscript{66,69} Due to the larger atomic size of Al atom than Si, the substitution of Al into SiO₂ framework causes a stronger compression of the Si–OH–Al bridge resulting in higher acidity. The more facile relaxation of the Al–O–P units counteracts this compression in SAPO giving rise to a lower acidity of BAS.

Besides the decreased framework Al content, there has also been significant debate on the role of extramframework Al (EFAI) species on the enhanced acidity of BAS.\textsuperscript{68,71,72} Previous theoretical studies have also demonstrated a pronounced acidity enhancement due to the presence of hard Lewis acid cations in close vicinity to BAS, e.g., in partially alkali and alkaline earth metal exchanged zeolites.\textsuperscript{73,74} For such alkali metal modified and EFAI-modified zeolites, the ΔE_ads values of bases (Table 1, FAU-47 vs FAU-Na vs FAU-EFAI, ΔE_ads[N(CH3)3] = −185 vs −199 vs −241 ~ −252 kJ/mol, and ΔE_ads[C6H5N] = −192 vs −212 vs −252 ~ −268 kJ/mol) show the following acid strength trend: FAU-47 < FAU-Na < FAU-EFAI. Both the Na cations and EFAI cationic species enhance the strength of the nearby BAS, and this promoting effect is much more significant for EFAI-containing zeolites. Such an effect has been earlier suggested to originate from the polarization of BAS by cationic species.\textsuperscript{75–77}

The results presented so far indicate that, even for faujasite-type materials in which all T sites are equivalent, the acid strength of BAS is affected by local variations in the framework composition as well as by the presence of extramframework species. This indicates that in practical zeolites the exact Al distribution, the Al content, and the presence of extramframework cations will add to the heterogeneity in the strength of the BAS.\textsuperscript{78,79}

Figure 3 presents the computed adsorption energies of different bases in FAU models as a function of the adsorption energies of pyridine. Pyridine adsors the strongest among the bases considered in this study. For all the other four bases, the adsorption energies correlate linearly with the ΔE_ads(C,H,N). Thus, it is expected that the calorimetric characterization of acid strength with these bases would give the same trend for faujasite zeolites. The slopes of the trendlines indicate that the sensitivity of these bases for probing acid strength follows the trend C,H,N > N(CH3)3 > NH3 > CH3CN > CO. A higher proton affinity of a base benefits proton transfer in the adsorption complex. CO and CH3CN with proton affinities of 594 and 779 kJ/mol, respectively, are only adsorbed by hydrogen-bonding interaction, while for NH3 (854 kJ/mol), N(CH3)3 (949 kJ/mol), and C6H5N (930 kJ/mol) with increased proton affinity, proton transfer occurs upon adsorption.

The dispersion interactions between guest molecules and zeolite walls are particularly important for adsorption in zeolites. For each guest molecule (Table 1), the dispersion contribution ΔE_ads(D) does not depend on the FAU model. The average values are −8, −16, −16, −45, and −44 kJ/mol for CO, CH3CN, NH3, N(CH3)3, and C6H5N, respectively. The dispersion interaction is strongly affected by the size of the base. For example, when the H atoms in NH3 are substituted by methyl groups as in N(CH3)3 (Figure 4), the dispersion contribution increases from −16 to −45 kJ/mol. For the same base, the dispersion interaction with the zeolite wall is independent of the acid strength, which may be due to the similarity of the local structure of BAS in FAU zeolites.

The effect of zeolite topology was studied by comparing the results obtained for CHA and MFI zeolite models with those for FAU-47. The BAS in MFI is located at the channel intersection (Figure 1, MFI), and the adsorption of bases can occur in both straight and sinusoidal channels (Figure S1). It is found that the adsorption energies of these bases in both locations are similar (Table S1), and here we only present the results of base adsorption in the sinusoidal channels (Table 1). Experimental studies reported that the adsorption heats for CO, CH3CN, NH3, N(CH3)3, and C6H5N on MFI zeolites are 29,80 110,81 145,155,82 205,82 and 200 kJ/mol,\textsuperscript{63} respectively. The experimental adsorption heats of ammonia on CHA-type zeolites with different Si/Al ratios are in the range 131–

![Figure 3. Scaling relations between the adsorption energies (ΔE_ads) of different base molecules in FAU zeolites.](image)

![Figure 4. Dispersion effect on adsorption energies of NH3 and N(CH3)3 in different zeolites.](image)
The calculated $\Delta E_{\text{ads}}$'s of bases in Table 1 cohere well with these experimental data, although in some cases the $\Delta E_{\text{ads}}$'s are slightly overestimated due to the inability of the PBE+D method employed in this study to reach chemical accuracy in adsorption energy calculations. The $\Delta E_{\text{ads}}$'s of CH$_3$CN, NH$_3$ and N(CH$_3$)$_3$ (Table 1) indicate that the acid strength (defined as the ability to protonation of a base) increases as FAU-47 < CHA < MFI, consistent with early theoretical work employing CH$_3$CN to probe the acid strength in high-silica zeolites. The dispersion contributions vary significantly for different framework structures, and this is particularly notable for the bulky base (Table 1). As shown in Figure 4, the dispersion-uncorrected adsorption energies ($\Delta E_{\text{ads}}$) of NH$_3$ still produce the same acidity trend as $\Delta E_{\text{ads}}$ because the influence of $\Delta E_{\text{ads}}$ (D) is only minor. However, for the bulky N(CH$_3$)$_3$ probe, the absence of the dispersion corrections changes the acid trend predicted by the $\Delta E_{\text{ads}}$ of N(CH$_3$)$_3$ (Figure 4). The results suggest that the effect of dispersion forces should be carefully considered when determining the acidity trends by adsorption heat of bases.

### 3.2. Chemical Bonding in Zeolites

Next, we compared the PDOS and COHP for the free zeolite BAS and the acid site interacting with CO and CH$_3$CN. Figure 5 shows results obtained for the hydroxyl group of BAS in FAU-47. Two PDOS domains can be distinguished below the Fermi level, namely the PDOS domain dominated by the occupied O(2s) atomic orbital (around $-21$ eV) and the PDOS domain dominated by the occupied O(2p) atomic orbitals (from $-10$ to the Fermi level). Above the Fermi level, the unoccupied PDOSs are dominated by the H(1s) atomic orbital. Figure 5b shows the bonding area below the Fermi level and it includes two regimes, namely, the interaction between H(1s) and O(2s) and the interaction between H(1s) and O(2p). There is no interaction between H(1s) and O(2p), because the orbital symmetries do not match. The antibonding feature is located on the H(1s) atomic orbital mainly above the Fermi level, which strongly overlaps with the SiO and AlO unoccupied antibonding electron conduction band regimes (Figure S2). The strong contribution of the O(2s) and O(2p) interaction in the antibonding OH bond regime is indicative of the significant hybridization.

We carried out a similar chemical bonding analysis for the adsorption complexes of CO and CH$_3$CN (Figure S3). Because of the requirement of orbital symmetry matching, only $\sigma$ orbitals contribute to the bonding and antibonding interaction for these probes. The chemical bonding interaction in CO adsorption complex can be described as a weak electron donation from the CO $\sigma$ electron density (Figure S3b, $\Delta \sigma$ $(-23$ eV), $4\sigma$ $(-8$ eV), and $5\sigma$ $(-3$ eV) in the Supporting Information) into the antibonding unoccupied OH bond. This leads to the perturbation of the OH and CO bonds, respectively, resulting in a red shift of the OH stretch and a blue shift of the CO stretch consistent with infrared spectroscopy experiment. In the CH$_3$CN adsorption complexes, the strongest bonding and antibonding interactions below the Fermi level are located between $-10$ and $-5$ eV (Figure S3d), corresponding to the interaction of the lone pair orbital in CH$_3$CN with the BAS. The highest occupied molecular orbital (HOMO) of CH$_3$CN (around $-2$ eV) has no interaction with the BAS because of the orbital symmetry mismatch. The stronger adsorption of CH$_3$CN compared with CO is reflected by a stronger bonding interaction between H and N than that between H and C. This also results in a stronger perturbation of OH in the BAS, giving rise to a much larger red shift of OH vibrational frequency in CH$_3$CN adsorption complex observed in the experiment.

Base adsorption methods are widely used to titrate the number of protons in zeolites, and the desorption temperature is an indicator for the acid strength. There are conflicting opinions in the literature whether adsorption energies or desorption temperatures are adequate measures of proton acidity. Alternatively, spectrometric methods are used to probe the strength of proton sites. It has been recommended to use the shifts of OH frequencies as the acidity measures when perturbed by CO and especially acetonitrile as such probes. Here we study the relation between the adsorption energies of probe molecules and changes in bond strengths as determined by the bond order (BO) calculations. As the basicity of CO is low, the variations in zeolite acidity do not affect the BOs of OH and HC bonds in the corresponding adsorption complexes (Table S2). With increasing acid strength of zeolite models, the interaction between the terminal N atom in CH$_3$CN and the proton becomes stronger with a simultaneous weakening of the OH bond in BAS. For FAU zeolites the values of BO(HN) and BO(OH) display the same trend of acid strength as determined by the $\Delta E_{\text{ads}}$ of CH$_3$CN (Figure 6, Table S2). However, MFI and CHA zeolites do not follow the trend of FAU. For example, the values of BO(HN) and BO(OH) in CHA are similar to those in FAU-47, indicating their similar intrinsic acid strength, but the adsorption energy of CH$_3$CN is much larger in CHA than in FAU.
FAU-47. The local structure of acid sites varies in topologically different zeolites, which results in very different van der Waals interactions (−35 kJ/mol in CHA vs −15 kJ/mol in FAU-47 for CH₃CN adsorption). Thus, for different zeolite structures the chemical bonding changes are better probes for intrinsic acid strength, because they do not contain additional physical adsorption effects that are sometimes significantly contributing to the adsorption energies of probe molecules.

3.3. Catalytic Reactivity. We further analyzed the dependency between acidity and reactivity of zeolites using protonation of isobutene as a model reaction. The acid strength was determined by the adsorption energy of NH₃, which has been successfully applied as a reactivity descriptor for catalytic conversion such as the methanol−olefin reactions and protolytic alkane cracking.¹⁷,¹⁸,⁴⁵ The reaction of isobutene with BAS may yield isobutoxy or tert-butoxy intermediates depending on which position of the double bond is protonated.⁹⁰,⁹¹ Here we only consider the formation of tert-butoxy, which is the kinetically preferred pathway (Figure 7a).

The formation energies (ΔE) of the respective π adsorption complex (Ads-C₄), transition state (TS-C₄), and tert-butoxy species (Alkoxy-C₄) with reference to the free zeolite model and gas-phase isobutene are listed in Table 2. For all the FAU models, the dispersion contributions (ΔE(D)) to the ΔE of Ads-C₄, TS-C₄, and Alkoxy-C₄ increase sequentially. For each reaction intermediate or TS, the variation of ΔE(D) among different FAU models is only minor. In MFI and CHA zeolites the dispersion interactions have a much stronger stabilization effect for all the intermediates and transition states along the reaction path of isobutene transformation (Table 2).

Our results suggest that, despite the substantial effect of the dispersive stabilization of the zeolite framework on the computed barriers for isobutene protonation, dispersion itself does not depend on the acidity of zeolites with the same topology and is therefore likely determined by the pore structure of the zeolite. In FAU zeolites the activation barriers with (ΔE(total)) and without [ΔE(total)−ΔE(D)] dispersion corrections give very similar slopes of the fitting trend (Figure 7b), indicating the independency of the dispersion effect on the acid strength. The decreased intercept of the trendline of dispersion-corrected activation barriers implies that the dispersion interaction decreases the reaction barriers by around 10 kJ/mol for all FAU zeolites. In CHA the effect of dispersion interaction is even stronger; it decreases the barrier by 29 kJ/mol. However, for MFI the inclusion of dispersion effects raises the barrier by 9 kJ/mol. The isobutene protonation occurs at the intersection of sinusoidal and straight channels in MFI (Figure S4), and the optimized structures show that the tert-butyl fragment in the TS is bent to the straight channel to a larger extent than the isobutene fragment in the π complex. This may lead to a decreased dispersion stabilization effect on the TS compared with the π complex, because for guest molecules the sinusoidal channel provides a better confinement and, accordingly, dispersion stabilization than the straight channel with a larger cavity (Table S1). The results suggest that the effect of the dispersion interactions on the catalytic reaction...
The corresponding dispersion components of $\Delta E$ are indicated as $\Delta E(D)$. Activation barriers ($\Delta E^\ddagger_{\text{total}}$) and respective dispersion-uncorrected values ($\Delta E^\ddagger(D)$) are listed separately. As the estimated energy barriers in EFAI-containing models are even lower than 5 kJ/mol (Table S3), we ignore these models here to minimize the methodological error from DFT calculations.

4. CONCLUSION

In summary, the scaling relations for zeolite acidity and catalytic reactivity were explored using a variety of zeolite models. The acid strength of faujasite (FAU) zeolites was tuned by varying framework composition or introducing extraframework cations. The properties of CHA and MFI were further compared with FAU to account for the effect of zeolite topology. For FAU zeolites the adsorption energies of bases such as CO, CH$_3$CN, NH$_3$, N(CH$_3$)$_3$, and C$_5$H$_5$N give the same trend of acid strength, and the sensitivity of these bases for probing acidity follows the trend C$_5$H$_5$N $>$ N(CH$_3$)$_3$ $>$ NH$_3$ $>$ CH$_3$CN $>$ CO. In the adsorption complexes the dispersion interaction with zeolite wall is stronger for bases with larger molecular size, and the dispersion contributions are independent of acid strength in topologically similar zeolites.

COHP analysis provides a detailed molecular orbital picture of adsorbed bases on the BAS. The orbital interaction only occurs when symmetry matches. For CO and CH$_3$CN adsorption, strong $\sigma$ donation from guest molecules to the BAS was observed. The bond order parameters derived for the CH$_3$CN adsorption complex are a useful descriptor for the intrinsic acid strength of FAU zeolites, which gives a consistent acidity trend as probed by the adsorption energies.

For MFI and CHA with different framework topologies, the dispersion contributions for the stabilization of guest molecules vary significantly from FAU zeolites, particular for bulky bases. MFI and CHA zeolites do not follow the scaling trend of FAU zeolites, and the scaling relations derived from the adsorption energies of bases and related bond order parameters seem only applicable in zeolites with the same topology and similar local structures of acid sites. The catalytic reactivity of isobutene conversion into alkoxy species were evaluated for different zeolite models. The acid strength determined by adsorption energies of NH$_3$ gives good correlation with the activation barriers of isobutene protonation in FAU zeolites. The effect of dispersion interaction on activation barriers varies for different zeolite framework types but shows similarity for the same FAU

### Table 2. Formation Energies ($\Delta E$) of π Complex (Ads-C4), Carbenium-Ion-like Transition State (TS-C4), and Surface tert-Butoxy Species (Alkoxy-C4) with Respect to Free Model and Gas-Phase Isobutene (all energies are in kJ/mol)\(^{a,b}\)

<table>
<thead>
<tr>
<th>zeolite model</th>
<th>Ads-C4</th>
<th>TS-C4</th>
<th>Alkoxy-C4</th>
<th>activation barriers</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAU-47</td>
<td>$-73$</td>
<td>$-42$</td>
<td>$-73$</td>
<td>$30$</td>
</tr>
<tr>
<td>FAU-7</td>
<td>$-70$</td>
<td>$-27$</td>
<td>$-76$</td>
<td>$43$</td>
</tr>
<tr>
<td>FAU-2-4</td>
<td>$-69$</td>
<td>$-2$</td>
<td>$-34$</td>
<td>$67$</td>
</tr>
<tr>
<td>FAU-Fe</td>
<td>$-68$</td>
<td>$-24$</td>
<td>$-87$</td>
<td>$44$</td>
</tr>
<tr>
<td>FAU-Ga</td>
<td>$-71$</td>
<td>$-35$</td>
<td>$-81$</td>
<td>$36$</td>
</tr>
<tr>
<td>FAU-SAPO</td>
<td>$-68$</td>
<td>$-20$</td>
<td>$-71$</td>
<td>$49$</td>
</tr>
<tr>
<td>FAU-Na</td>
<td>$-75$</td>
<td>$-49$</td>
<td>$-66$</td>
<td>$27$</td>
</tr>
<tr>
<td>MFI</td>
<td>$-97$</td>
<td>$-62$</td>
<td>$-86$</td>
<td>$35$</td>
</tr>
<tr>
<td>CHA</td>
<td>$-97$</td>
<td>$-70$</td>
<td>$-27$</td>
<td>$72$</td>
</tr>
</tbody>
</table>

\(^{a}\)The stability of alkoxy species was evaluated by comparing the adsorption free energy of tert-butoxy (Table 2) with that of tert-butoxy (Table 2).

\(^{b}\)The formation energy of tert-butoxy (Table 2) suggests its lower stability in CHA than in other topologies, which may be due to the larger stabilization of guest molecules via van der Waals interactions.

\(^{c}\)This gives an indication that small-pore zeolites may bias the free carbocation more than the alkoxy species generated from the corresponding alkene.

\(^{d}\)The formation energy of tert-butoxy (Table 2) suggests its lower stability in CHA than in other topologies, which may be due to the larger stabilization of guest molecules via van der Waals interactions.

\(^{e}\)This gives an indication that small-pore zeolites may bias the free carbocation more than the alkoxy species generated from the corresponding alkene.
topology, and the steric effect between reactant and zeolite wall also represents one important factor determining the catalytic reactivity.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b08176.

Extended computational results, additional supporting data (PDF)

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**Notes**

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