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Ensemble of Active Acid Sites on Amorphous Silica-Alumina Surfaces for Catalytic Cracking

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Abstract:

Amorphous silica-alumina are critical materials in catalysis, particularly for Fluid Catalytic Cracking (FCC). However, the atomic scale understanding of the active sites has been challenging, because of the non-uniform atomic distribution and the material's amorphous nature. Here, we use density functional theory (DFT), machine learning potentials and sampling methods to investigate the relationship between structure and acidity in silica-modified alumina. Under FCC conditions, we predict an ensemble of acid sites with diverse local structures and a spectrum of acid strengths, including zeolite-like bridging Brønsted acid sites (BAS) and pseudo-bridging silanol BAS. This distribution is influenced by surface structure, Si coverage, and extent of hydroxylation, shaped by synthesis methods and reaction conditions. Experiments using a model Si-stabilized alumina catalyst confirm that Brønsted acidity increases with Si content, peaking at an optimal value before declining. These insights provide a foundation for designing efficient solid acid catalysts for industrial applications.

Introduction

Amorphous silica-alumina (ASA) are widely used in industrial applications due to their excellent mechanical and hydrothermal stability, as well as their micro and meso porous structure, which facilitates rapid diffusion of reactants and products^[1]. Furthermore, they can stabilize a variety of active materials dispersed on their surfaces^[2,3], making them effective supports for catalytic applications. Although supports in catalysis were historically considered to be inert, ASA are now well recognized for their influence on the activity and selectivity of catalytic cracking reactions^[4–8], which is a key process in converting heavy hydrocarbons into lighter, more valuable products. These combined properties make ASA an essential component in refining and petrochemical processes. The activity of ASA stems from their unique surface acid-base properties. The complex distribution of Al and Si atoms at the amorphous surface induces Lewis and Brønsted acidity through surface hydroxylation, which is different from that of bare alumina, silica surfaces, or crystalline aluminosilicates like zeolites^[9–13]. The systematic study of commercial ASA materials, as well as model materials such as Al₂O₃ on SiO₂ (Al/SiO₂) or SiO₂ on Al₂O₃ (Si/Al₂O₃), reveals that the surface exhibits multiple types of Brønsted acid sites (BAS)^[10,13–15]. More importantly, they display mild intrinsic acidity relative to the strong acidity in zeolites. The specific distribution and nature of the acid sites on the surface significantly influences catalytic performance^[16]. Therefore, there is a need to develop atomistic models that can help tailor the composition and structure of these materials in reaction conditions to optimize them for specific reactions. This is, however, highly challenging, primarily because of the non-uniform distribution of silicon and aluminum atoms as well as the material's amorphous nature. Current models in the literature are highly simplified.

The exact origins of the acidity of ASA are indeed a topic of active research, with several structural models being proposed^[17,18]. Hensen et al^[11] reported the presence of very small number of zeolite like Brønsted acid sites (BAS)

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(<10 μmol/g), weak BAS whose structure is unclear (50–150 μmol/g) and a high concentration of aluminols and silanols (200–400 μmol/g). Further, they proposed that strong zeolite-like BAS are the acid site for bifunctional n-heptane hydro-conversion. However, the vibrational properties of CO and pyridine, which were used for quantification are not specific to a given ASA surface site, limiting the precision of the analysis^[19,20]. Additionally, the diversity in structure and acidity of ASA, make it challenging to gain fundamental insights^[13]. On the other hand, Trombetta et al.^[21] first proposed that the strong BAS on ASA can be a silanol adjacent to a Lewis-acidic Al center. Chizallet and Raybaud refined this idea through molecular modelling and coined the term pseudo-bridging silanol (PBS) for such motifs^[22]. PBS are essentially silanols near an undercoordinated surface Al species^[20]. Subsequently, Valla et al.^[23] corroborated the presence of PBS sites on the model Si/Al₂O₃ ASA surface using dynamic nuclear polarization surface enhanced NMR spectroscopy (DNP SENS) and proposed that the acceptor Al atom in PBS is likely in tetrahedral coordination, while the Si is also covalently bonded to other undercoordinated Al. Recently, Salvia et al. used ¹H MAS NMR spectrum to measure H-Al distance in the active sites for cracking reaction on ASA and reported it to be comparable to the BAS in zeolites and far too short to represent PBS. Huang et al. recently broadened the structural picture of acidity in amorphous silica-alumina. Using ultra-high-field (35.2 T)²⁷Al{¹H} D-HMQC NMR, they directly detected both zeolite-like bridging groups and pseudo-bridging silanols, confirming that multiple Brønsted site types coexist on the surface^[24]. Their studies also revealed a motif in which a single silanol interacts with two neighboring Al centres^[25], underscoring the structural complexity that can arise in ASA. The lack of consensus among these studies further confirms the challenge in establishing a direct correlation between structure and catalytic activity. Moreover, the acid site strength and distribution are influenced by various factors, including synthesis, pretreatment, and reaction conditions, presenting challenges in development of an accurate atomistic model^[26,27]. Although a macroscopic correlation between increasing Si content and rising Brønsted acidity has been reported consistently^[28–30], these studies stop short of providing an atomistic model that can accommodate the full diversity of acid sites and predict their individual reactivity. Addressing that gap is the central aim of the present work.

In this study, we therefore aim to elucidate the structural diversity of acid sites on aluminosilicates by studying the model Si/Al₂O₃ surface using DFT calculations with exhaustive sampling of structural configurations. The choice of the model is motivated by the similarity of Si stabilized γ-Al₂O₃ to the spinel phase^[31] of Al-Si, which was observed in the industrial FCC catalyst^[32,33] derived from kaolin clay^[34]. Additionally, studies in the literature suggest that Si/Al₂O₃ is more active than the Al/SiO₂ model and commercial ASA sample^[12]. However, the ASA formed using well defined experimental procedures are also heterogeneous at their surface and difficult to model. Traditional approaches face limitations in accurately representing such systems due to the wide variety of structurally and chemically distinct acid site environments^[35]. Previous computational studies by Raybaud and coworkers^[19,20,22] investigating the acid properties of Si/Al₂O₃ primarily employed single, specific structural models to represent the material. While these models provide valuable insights into localized phenomena, they oversimplify the system by neglecting the heterogeneity of the surface. As a result, they offer a limited perspective on the broader range of acid sites.

Two primary challenges arise while fully representing the heterogeneous surface: first, the high computational cost of DFT, and second, the difficulty in exploring all possible structural configurations. To address the high computational cost of DFT, we develop machine learning interatomic potentials (MLIPs) derived from E(3)-equivariant deep neural networks^[36]. To address the sampling limitations, we implement a graph-based enumeration scheme^[37] to generate unique structures and use a grand canonical basin-hopping^[38] approach to further sample configurations under conditions relevant to FCC. MLIPs calculate energies close to DFT accuracy with a computational cost decreased by a factor of 10⁴, hence enabling the use of extensive configuration sampling methods. To our knowledge, this combination of method has not been used before for Si-doped Al₂O₃.

Our calculations predict the formation of a diverse ensemble of acid sites on Si-doped γ-Al₂O₃ surfaces, including both zeolite-like bridging Brønsted acid sites (BAS) and the previously proposed PBS sites. This finding supports a more dynamic view of Brønsted acidity, conceptualized as a continuous spectrum rather than distinct, discrete categories which was not captured by previous modelling studies. Unlike pristine zeolites, which exhibit strong, well-defined BAS, the acid strength of these sites on Si-doped γ-Al₂O₃ is weaker and heterogenous. The distribution and strength of these acid sites are influenced by several key factors, including surface structure, Si coverage, and the extent of hydroxylation. We highlight that optimal acidity is achieved at intermediate levels of Si coverage. At these levels, the formation of strong BAS is maximized. Further Si incorporation results in a decline in acid strength due to the prevalence of weakly acidic silanol groups. To validate the theoretical predictions, we compared our results with experimental models of Si-grafted γ-Al₂O₃ reported in the literature. Additionally, we compared with the

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cracking performance of model catalyst tested using the standard Advanced Cracking Evaluation (ACE™) unit, as conducted by BASF. The results revealed a correlation between catalytic cracking activity and Bronsted acidity.

Results and Discussion

Surface Models for Si/Al₂O₃

The preparation of Si/Al₂O₃ can involve grafting Si onto γ -Al₂O₃ either in a liquid medium (chemical liquid deposition, CLD) or a gas phase (chemical vapor deposition, CVD) (Figure S2). The condensation process is essentially similar to silicic acid (Si(OH)₄) exchanging with the OH of γ -Al₂O₃ and the exchange energy is defined as ΔE_{ex} (equation S1). The extent of Si deposition on the alumina surface depends on the surface termination and degree of hydroxylation of γ -Al₂O₃, leading to either isolated Si-O-Al linkages or more extensive poly-silicic networks. Our calculations of the exchange energies (ΔE_{ex}) for the most stable structures on the hydroxylated (001) and (110) surfaces (Figure 1a) indicate that initial Si deposition is energetically favored on the (001) surface, consistent with experimental observations^[16]. Furthermore, our findings show that Si(OH)₄ primarily exchanges with surface Al-OH groups, but if the surface becomes sterically blocked by previously exchanged Si(OH)_x species, it will then exchange with OH on the Si themselves. At moderate to high Si coverages, the difference in exchange energy (ΔE_{ex}) between the (001) and (110) surfaces become minimal. Specifically, at a coverage of $\theta_{Si} \sim 4.4 \text{ nm}^{-2}$, ΔE_{ex} differs by only 0.01 eV. Structurally, they are quite similar at this coverage, with the (001) surface forming two Si(OH)_x dimers (Figure 1b), while the (110) surface forms one Si(OH)_x dimer (Figure 1c). These results suggest that at higher coverages, both the (001) and (110) surface terminations are relevant in understanding the surface interactions of Si with alumina.

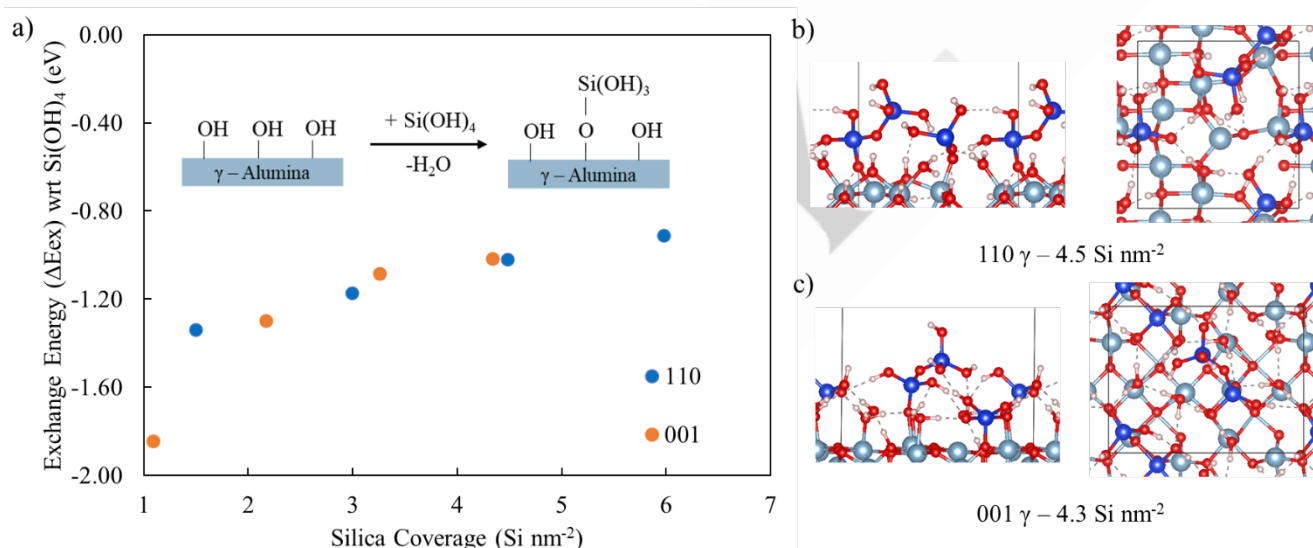


Figure 1: (a) The exchange energy (ΔE_{ex}) for Si(OH)₄ is plotted as a function of Si coverage for (001) (orange points) and (110) (blue points) on the γ -Al₂O₃ surface. We use the gas phase DFT energies for H₂O and Si(OH)₄ species as references. (b) Top and side view of 3 Si(OH)₄ exchanged on (110) γ -Al₂O₃ surface. (c) Top and side view of 3 Si(OH)₄ exchanged on (001) γ -Al₂O₃ surface. The light blue, dark blue, red, and white balls represent Al, Si, O, and H atoms respectively. The solid black line represents the unit cell, and the dotted black line represents H-Bonds. Atoms in the bottom layers are hidden for better readability.

Further thermal treatments are necessary in the preparation to promote additional condensation of Si(OH)_x groups, leading to the formation of more Si-O-Al bonds and mixing of Si near the surface. Additionally, Mouat et al.^[39] found that the preparation method of Si/Al₂O₃ catalysts has less influence on the final structure of the silanol sites than the post-treatment conditions. They observed that the concentration of isolated silanols increases after calcination. Higher temperatures facilitate surface reconstruction, enabling the mixing of Al and Si atoms. Herein, we chose to add SiO₂ to bare γ -Al₂O₃, and then partially hydroxylate the structures according to reaction conditions, instead of dehydroxylating Si exchanged γ -Al₂O₃ models (Figure S3). This approach is computationally simpler, and we confirmed that the resulting structures are equivalent for both methods (Figure S3).

This initial model serves two important purposes. First, it corrects misleading conclusions that might arise from considering only the direct adsorption of SiO₂ on dehydrated surfaces. As shown in Figure S4a, the adsorption energy of SiO₂ on pristine, non-hydroxylated γ -Al₂O₃ is endothermic, especially on the (001) surface. This could falsely suggest that the (001) facet is incapable of Si-O-Al bond formation. Secondly, we validate the assumption

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introduced by Chizallet et al.^[22] that direct SiO₂ deposition can be interpreted as a thermally induced dehydroxylation of surface-bound Si(OH)_x species.

The undoped surface of γ -Al₂O₃ has pairs of Lewis acid (Al^{δ+}) and Lewis base (O^{δ-}) sites. The non-hydroxylated (110) surface (75% twofold unsaturated octahedral Al and 25% onefold unsaturated tetrahedral Al) exhibits stronger Lewis acid sites than the (001) surface (onefold unsaturated octahedral Al)^[40,41] (Figure 2a,f). This difference in acidity leads to stronger adsorption of SiO₂ on the (110) surface relative to the (001) surface (Figure S4a). Upon adsorption and reconstruction, Si creates new Lewis acid (Al^{δ+} or Si^{δ+}) and Lewis base (O^{δ-}) sites on the surface. On the (110) surface, the Si can easily promote reconstruction of the Al and O atoms to accommodate Si on the unsaturated atoms in a tetrahedral geometry (Figure 2b,c). Continued SiO₂ adsorption results in the formation of Si-O chains on the surface, linked by Al^{IV} tetrahedral atoms (Figure 2d,e).

In contrast, the (001) surface is less reactive, making the initial adsorption of SiO₂ less favorable as Si cannot easily reconstruct the surface Al and O atoms leading to higher energy distorted tetrahedral geometry (Figure 2g,h,i). As Si coverage increases, Si-O chain formation also occurs on the (001) surface through the under coordinated Al^V. Despite this, the adsorption energy remains significantly lower than on the (110) surface, suggesting the possibility of Si migration from the (001) surface to the (110) surface to achieve a more stable configuration. Furthermore, Si consistently displaces Al atoms, leading to new Al coordination states (Al^{IV}, Al^V, and Al^{VI}) and modifying the catalytic environment near the surface.

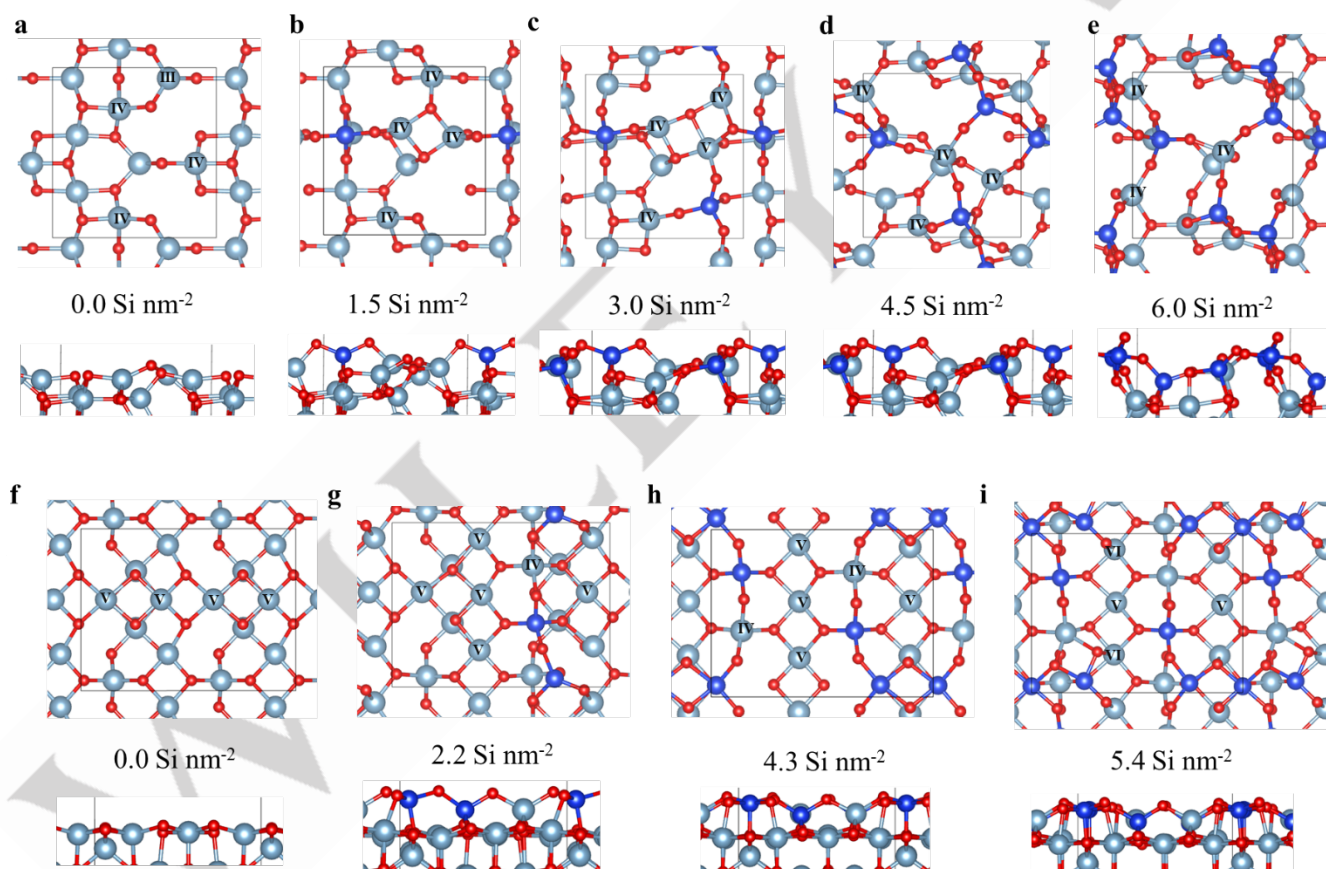


Figure 2: (a-e) The top and side view of growth of SiO₂ on (110) γ -Al₂O₃ surface, with increasing Si coverage from 0.0 Si nm⁻² to 6.0 Si nm⁻² (f-i) The top and side view of growth of SiO₂ on (001) γ -Al₂O₃ surface, with increasing Si coverage from 0.0 Si nm⁻² to 5.4 Si nm⁻². The light blue, dark blue, red, balls represent Al, Si, and O atoms respectively. The black roman numerals indicate the co-ordination of surface Al atoms. The solid black line represents the unit cell, and the atoms/bonds in the bottom layers are hidden for better readability.

Subsequent hydroxylation of the SiO₂ modified surface to determine surface composition and structure in reaction conditions creates a vast array of possible configurations, as water (H₂O) can dissociatively adsorb on several different sites^[42]. To manage and accelerate calculations, we performed DFT calculations on a selected dataset of structures. We used this dataset to train two MLIPs, each tailored for the (110) and (001) surfaces. We conducted

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DFT calculations at lower water coverages and used the trained MLIPs to predict energies at higher water coverages. Full details on dataset curation, MLIP settings, accuracy, and validation are provided in the Supporting Information.

To understand hydroxyl coverage and the density of Brønsted acid sites (BAS) under realistic experimental conditions, we generated phase diagrams as a function of water chemical potential within a grand canonical ensemble framework. Higher chemical potentials of gas-phase water correspond to higher hydroxyl coverage on the surface. We highlighted two specific conditions: (1) $T = 700^\circ\text{C}$ and $P_{\text{H}_2\text{O}} = 0.3$ bar ($\Delta\mu_{\text{H}_2\text{O}} = -1.52$ eV), and (2) $T = 550^\circ\text{C}$ and $P_{\text{H}_2\text{O}} = 1.2$ bar ($\Delta\mu_{\text{H}_2\text{O}} = -1.05$ eV), representing typical conditions in the FCC regenerator and at the reactor entrance (2 wt% H_2O mixed with 98 wt% gas oil at zero conversion), respectively.

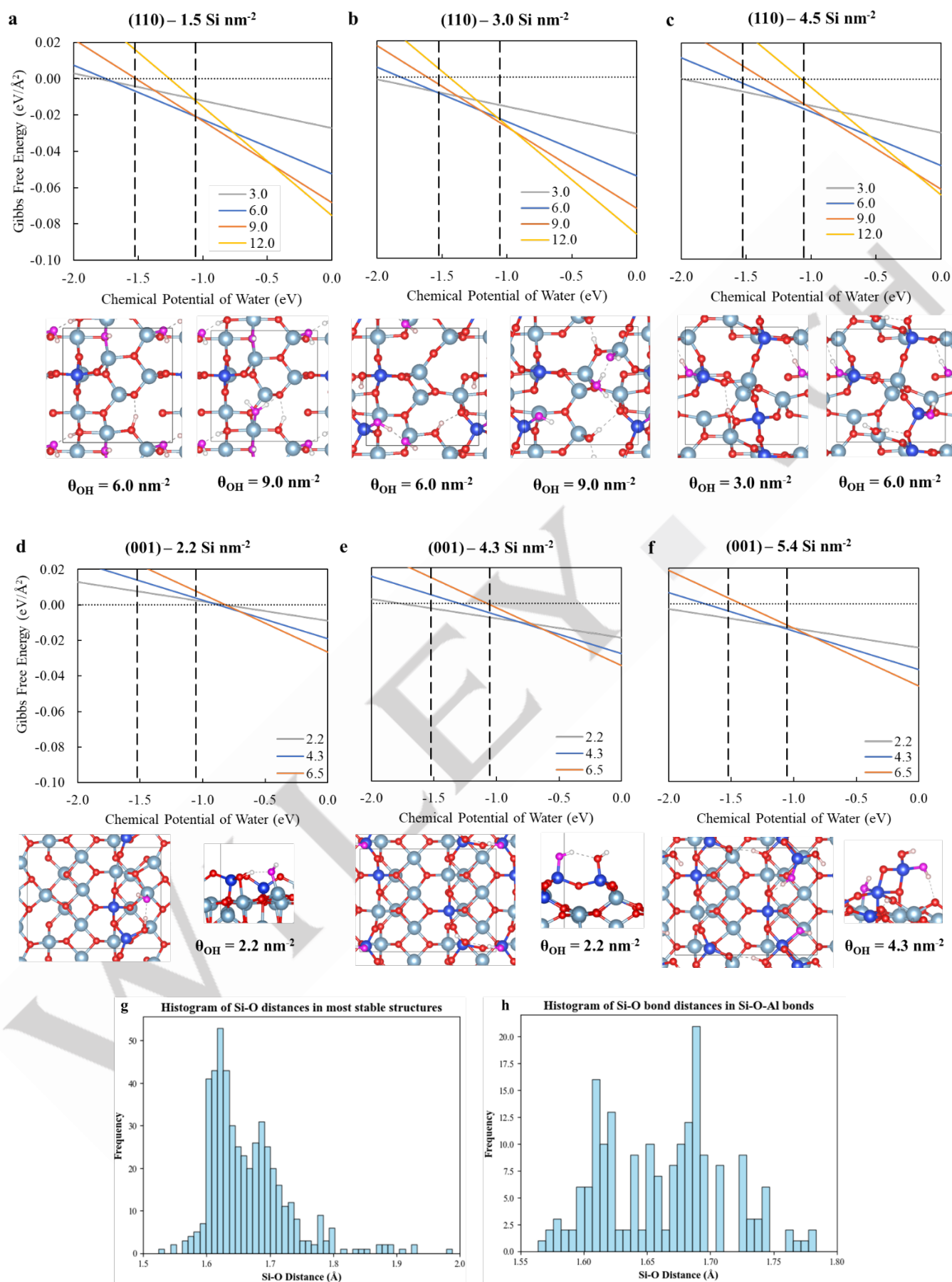
The undoped $\gamma\text{-Al}_2\text{O}_3$ (001) surface shows minimal hydroxylation at high temperatures, while the (110) surface retains significant hydroxyl coverage (Figure S4b)^[43]. However, introducing Si dramatically alters this behavior: the (001) surface becomes more prone to water adsorption with respect to undoped $\gamma\text{-Al}_2\text{O}_3$ (001), whereas the (110) surface becomes less susceptible to it (Figure 3) with respect to undoped $\gamma\text{-Al}_2\text{O}_3$ (110). On the (110) surface, Si preferentially adsorbs at reactive sites that typically dissociatively adsorb water, blocking these sites and reducing hydroxyl coverage. Figure 3a-c demonstrates that increasing Si content under FCC conditions results in a consistent decline in hydroxyl coverage on the (110) surface. Initially, water dissociatively adsorbs on exposed Al atoms, but with greater Si incorporation, both zeolite-like bridging Brønsted acid sites (BAS) and pseudo-bridging silanol (PBS) sites emerge. At high Si coverages (≥ 6.0 OH nm⁻², Figure S5), the surface becomes dominated by silanol groups, as Al atoms are progressively buried beneath Si-O layers. To support this claim we calculated the occurrence of Si-O-Al bonds vs Si-O-Si bonds with increasing Si coverage and reported in Figure S5.

In contrast, on the (001) surface, Si adopts a less stable, non-tetrahedral geometry, which readily binds hydroxyls and stabilizes into a tetrahedral geometry. Specifically, at comparable Si coverages, the average O-Si-O bond angle is 109.15° for the (110) surface (4.5 Si nm⁻²) and 107.7° for the (100) surface (4.3 Si nm⁻²), indicating a deviation from ideal tetrahedral coordination for the latter. This leads to an increase in hydroxyl coverage with increasing Si content (Figure 3d-f), unlike the trend observed on the (110) surface. The formation of silanols on the (001) surface at high Si coverages aligns with computational^[22] and experimental^[16] findings. However, at high hydroxyl coverages (high $\Delta\mu_{\text{H}_2\text{O}}$), we predict the formation of both zeolite-like bridging sites and PBS sites on the (001) surface.

In zeolites, Brønsted acid sites (BAS) are generated by the charge imbalance caused by the incorporation of Al into the Si framework. In contrast, the structures investigated here are charge-neutral, and the BAS arise from surface undercoordination and suboptimal bonding environments. The Si-O-Al bond distances display notable variability (Figure 3g,h), influenced by the specific type of acid site, the degree of Si coverage, and the surface termination. Additionally, we observe a broad distribution of Si-O-Al angles (Figure S10), consistent with prior DFT studies of amorphous silica alumina systems^[20,44]. Together, this variability highlights the intricate interplay between local geometric and electronic factors that govern the formation and properties of these acid sites.

It is worth noting that the diversity in environments surrounding the Brønsted acid sites (BAS) results in a range of vibrational frequencies, as shown in Table S3. Assigning specific frequencies to structures is challenging due to the broad hydrogen-bonding effects among hydroxyl groups^[43], which may contribute significantly to the experimental frequency range of $2800\text{--}3850$ cm⁻¹^[20].

To test the robustness of our protocol, we recalculated the (110) surface with a supercell twice the lateral dimensions of the original model. All calculations were performed using the machine learning potentials (MLPs) developed in the previous section, trained on structures with a smaller unit cell. Full structural details and energetics are provided in the Supporting Information (Figure S6). Although the larger cell leads to slightly greater surface disorder, closer to the amorphous limit, the key trends remain unchanged. At low Si loading (1.5 Si nm⁻²), the surface is dominated by isolated aluminols and a small fraction of molecularly adsorbed H_2O ; no bridging Si-OH-Al groups are present. At intermediate Si loading (3.0 Si nm⁻²), the interfacial Si-OH-Al linkages become prevalent, giving rise to zeolite-like bridging OH groups and the stronger Brønsted acid sites. These results mirror those obtained with the smaller unit cell.



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Figure 3: (a-c) Grand canonical phase diagram for (110) γ - Al_2O_3 surface, with increasing Si coverage from 1.5 Si nm^{-2} to 4.5 Si nm^{-2} . (d-f) Grand canonical phase diagram for (001) γ - Al_2O_3 surface, with increasing Si coverage from 2.2 Si nm^{-2} to 5.4 Si nm^{-2} . The dotted black lines highlight two specific conditions: (1) $T = 700^\circ\text{C}$ and $P_{\text{H}_2\text{O}} = 0.3 \text{ bar}$ ($\Delta\mu_{\text{H}_2\text{O}} = -1.52 \text{ eV}$), and (2) $T = 550^\circ\text{C}$ and $P_{\text{H}_2\text{O}} = 1.2 \text{ bar}$ ($\Delta\mu_{\text{H}_2\text{O}} = -1.05 \text{ eV}$). The legend in each graph represents the coverage of OH in (OH nm^{-2}). The top view of the most stable configuration at the experimental condition is depicted below the graph. The light blue, dark blue, red, pink balls represent Al, Si, O, O from H_2O atoms respectively. The solid black line represents the unit cell, and the atoms/bonds in the bottom layers are hidden for better readability. (g) Histogram of Si-O bond distances in the most stable structures for (110) and (001) surfaces. (h) A subset of (g), where only the Si-O bond distances in a Si-O-Al bond is present.

Acid Sites on $\text{Si}/\text{Al}_2\text{O}_3$

Brønsted acid strength can be assessed using density functional theory (DFT) either using deprotonation energy (DPE)^[45] or binding energy (BE) of a base molecule such as ammonia^[15], pyridine^[11], or lutidine^[20]. While DPE calculations provide a direct measurement of intrinsic acid strength, they are prone to artifacts in periodic DFT simulations. In contrast, BE calculations avoid these artifacts due to their inherent charge neutrality. Binding energy, however, is influenced by additional factors such as van der Waals interactions and hydrogen bonding within the local surface environment. In this study, we therefore used ammonia (NH_3) BE to probe acid strength. We would like to note that NH_3 FT-IR spectroscopy is generally not preferred for experimental characterization of acid sites due to overlapping absorption bands and the potential for ammonia decomposition under certain conditions^[46]. We chose NH_3 for our computational studies due to its smaller size and lower computational cost, which allows easier convergence and statistical sampling across many configurations. Importantly, we restrict our calculations to a single NH_3 molecule per site. This avoids the complexities associated with NH_3 clustering, which has been observed previously^[47,48]. By maintaining a one-to-one interaction model, we enable a more consistent comparison of acid strengths across the structurally diverse ensemble of surface sites. To ensure reliability, we also performed comparative BE calculations using the more commonly used pyridine as a probe, detailed in Figure S7. Our findings can be directly compared with NH_3 BE on well-characterized acid sites in zeolites³⁵, which serve as a reference standard.

The undoped γ - Al_2O_3 surface presents aluminol groups, which exhibit relatively weak Brønsted acidity. This is evidenced by ammonia binding energies (ΔE_{NH_3}) that do not exceed -75 kJ/mol . Similarly, we evaluated the ΔE_{NH_3} for silanol groups on hydroxylated amorphous SiO_2 , using the structural model proposed by Comas-Vives et al.^[49]. These binding energies fell between -50 to -77 kJ/mol and didn't lead to complete H^+ transfer to NH_3 , confirming the inherently weak acidity of the silanol groups. For Si-doped γ - Al_2O_3 , isolated silanols and aluminols also show ΔE_{NH_3} values between -20 kJ/mol and -80 kJ/mol , akin to the weak acidity of pure alumina or silica. However, the Si introduces new types of acid sites, including zeolite-like bridging Brønsted acid sites (BAS) and pseudo-bridging silanol (PBS) site. These newly formed sites exhibit significantly higher acid strengths, with ΔE_{NH_3} ranging from -90 to -110 kJ/mol (Figure 4). In comparison, Brønsted acid sites in bulk MFI zeolites, exhibit ΔE_{NH_3} values between -133 and -160 kJ/mol , as reported by Hibbitts et al.^[50]. This indicates that while the BAS and PBS sites in Si-doped γ - Al_2O_3 are stronger than those in pure alumina or silica, they remain weaker than the bulk zeolite counterparts. Intriguingly, external BAS on the zeolite surface have been reported to exhibit ΔE_{NH_3} as low (in absolute value) as -110 kJ/mol ^[50], comparable to the strongest BAS found in Si-doped γ - Al_2O_3 .

Distinguishing between zeolite-like bridging Brønsted acid sites (BAS) (Figure 4b,d,f) and pseudo-bridging silanol (PBS) sites (Figure 4a,e) is experimentally challenging, as both fall within a similar range of ΔE_{NH_3} . This is consistent with the spectroscopic work of Maugé et al.^[51], who observed pyridinium bands that desorb over a broad 473 - 573 K range on $\text{Al}_2\text{O}_3/\text{SiO}_2$ ASA catalyst, evidence for a minority of very strong OH groups embedded in a larger population of weaker ones. Earlier work, based on a much narrower set of configurations, classified zeolite-like bridging Brønsted sites as uniformly stronger than pseudo-bridging silanols (PBS)^[52]. Our broader sampling shows that acidity spans a continuum, so rigid categories are misleading. We therefore treat Si-doped γ - Al_2O_3 as hosting an ensemble of Brønsted sites with diverse structures and electronic environments. This ensemble includes sites, such as water molecules adsorbed on Al near silanol groups (Figure 4c) and PBS sites where proton transfer is accompanied by the formation of a new Al-O bond (Figure 4a,e).

Interestingly, proton transfer is not always required for strong NH_3 adsorption. For example, Figure 4f illustrates a case where NH_3 binds strongly to a bridging BAS without the necessity of H^+ transfer. On the other hand, we also observe weak NH_3 binding on a bridging BAS (-84 kJ/mol) without proton transfer. This observation highlights a key insight, also observed by Leydier et al.^[20]: intrinsic acidity, while necessary for proton transfer, is not sufficient to guarantee strong binding. The driving force for deprotonation lies in the stabilization of the conjugate base formed during proton transfer and its interaction with the protonated basic molecule. Thus, in our case the stabilization of

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both the anionic site on the aluminosilicate surface and the NH_3 -derived NH_4^+ ion is critical to determining the binding strength.

The diverse Brønsted acid site structures in ASA underscore the complexity of their acid properties. To understand the changes in relative population and density as a function of silicon (Si) coverage, the degree of hydroxylation, and the specific surface terminations present during synthesis, we calculated the Boltzmann-averaged ammonia binding energy (ΔE_{NH_3}) for BAS under two distinct conditions that simulate typical FCC environments: regenerator conditions and reactor conditions. The ΔE_{NH_3} serve as a proxy for acid strength, where more negative values indicate stronger acidity (Figure 5). Boltzmann averaging allows a statistical consideration of the ensemble effect, accounting for the contributions of multiple configurations within a given silica coverage. For example, at low silica coverage (1.5 nm^{-2}) on the (110) surface, metastable bridging Brønsted acid sites are observed (Figure S9a). We use the term metastable to describe BAS configurations that are higher in free energy relative to the most stable hydroxylated structures identified under the same chemical potential conditions. These configurations correspond to local minima within our global sampling and are therefore only sparsely populated in the Boltzmann-weighted ensemble. Nevertheless, despite their low thermodynamic stability, such structures may contribute disproportionately to catalytic activity, a concept supported by Wischert et al.^[53], who reported similarly high-energy configurations on alumina. However, for most configurations, the probability of forming metastable structures is effectively zero. Furthermore, each structure has multiple Brønsted acid sites. Herein, we Boltzmann average over these sites as well.

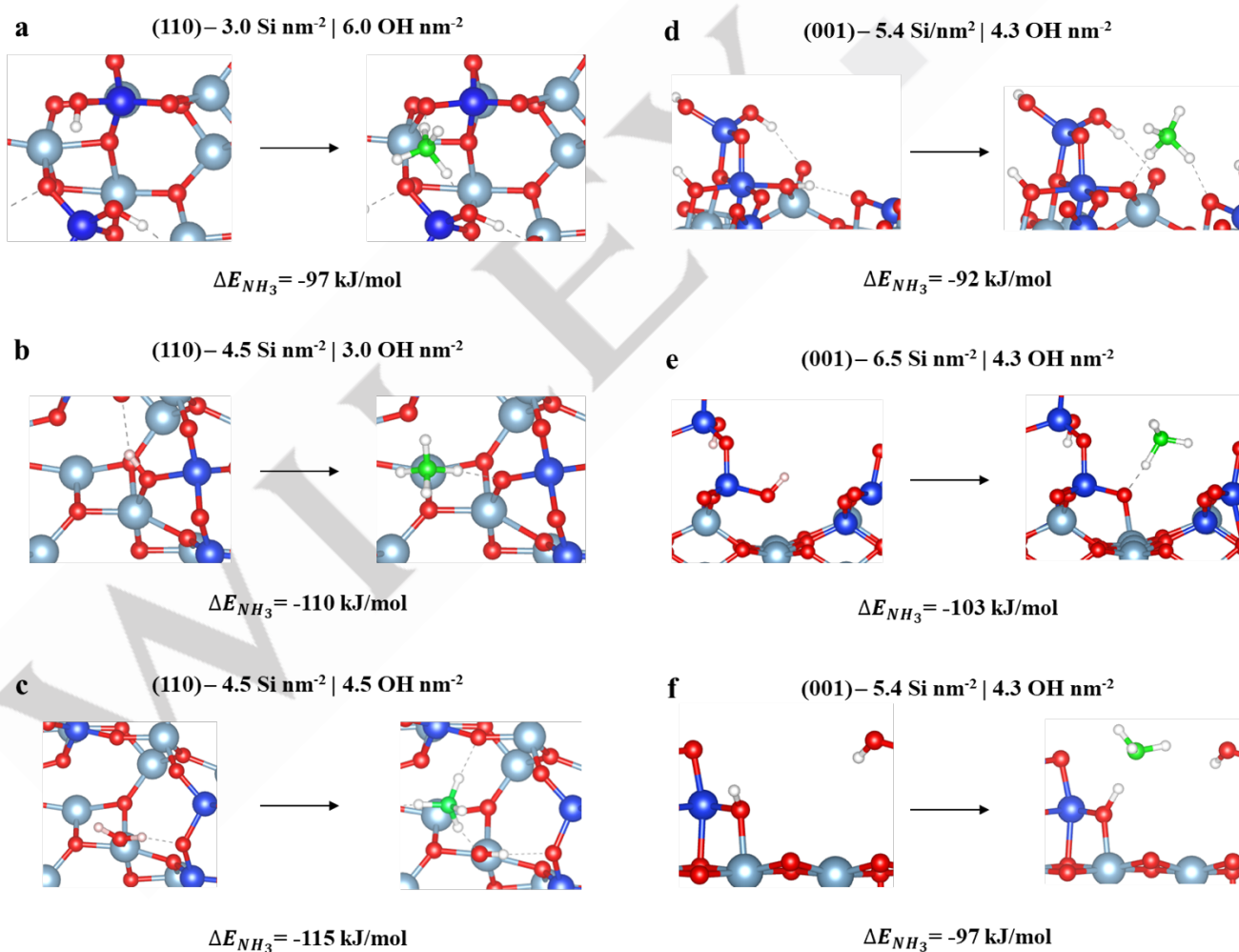


Figure 4: (a-c) Top view of NH_3 binding on (110) Si doped $\gamma\text{-Al}_2\text{O}_3$ surface. (d-f) Side view of NH_3 binding on (100) Si doped $\gamma\text{-Al}_2\text{O}_3$ surface. The Pseudo-Bridging Silanol Site is depicted in (a) and (e). Zeolite-like Bridging Site is depicted in (b), (d) and (f). The light blue, dark blue, red, white, and green colors represent Al, Si, O, H and N atoms respectively. The dotted black line represents H-bonds and the atoms/bonds in the bottom layers are hidden for better readability.

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For the (110) surface, the acid strength increases with rising Si coverage under both FCC regenerator and reactor conditions, reaching a maximum before declining. This increase is driven by the formation of both PBS and zeolite-like BAS. At intermediate Si coverages, these sites dominate, resulting in strong Brønsted acidity. However, beyond the optimal Si coverage, the surface becomes increasingly populated with silanol groups, reducing the overall Brønsted acid strength. The behavior of the (001) surface is slightly different from that of the (110) surface. Initially, the (001) surface is largely dehydroxylated, and as a result, it doesn't exhibit Brønsted acidity. Under FCC regenerator conditions (700°C), increased Si coverage results primarily in the formation of silanols, which, as expected, exhibit weak acidity. However, under FCC reactor conditions (higher hydroxylation), higher Si coverage leads to the emergence of both PBS and zeolite-like BAS, which contribute to enhanced Brønsted acidity, a regime not previously simulated. However excessive Si coverage eventually causes the surface to be dominated by Si-O chains and therefore silanols, once again diminishing the Brønsted acid strength.

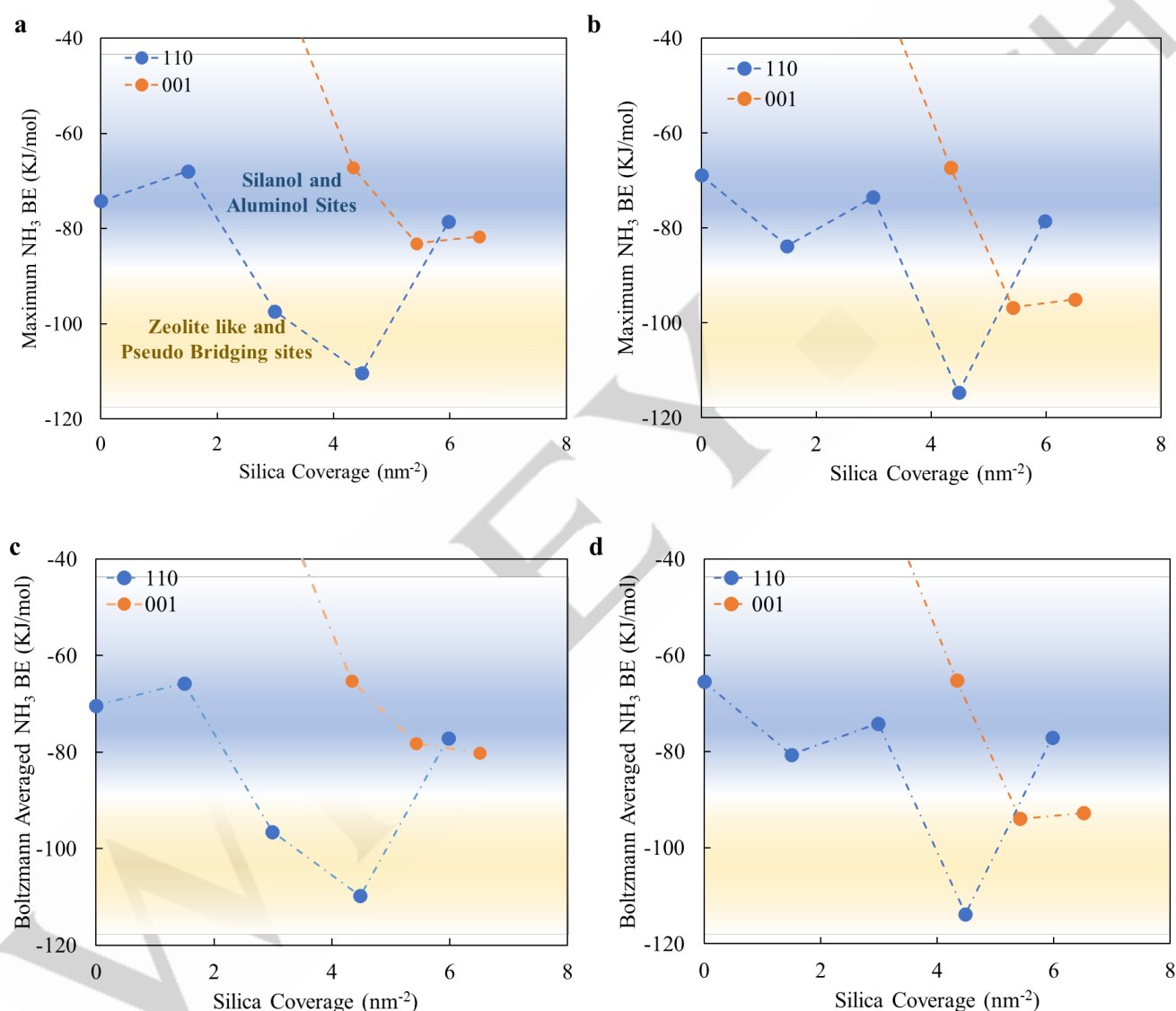


Figure 5: (a, b) The Minimum ΔE_{NH_3} for the most stable structure and the (c, d) Boltzmann averaged ΔE_{NH_3} for Brønsted Acid Sites is plotted for the (110) and (001) γ -Al₂O₃ surfaces, with increasing Si coverage. The hydroxyl coverage is determined by considering water chemical potential equal to (a, c) $T = 700^\circ\text{C}$ and $P_{H_2O} = 0.3$ bar (FCC regenerator conditions; $\Delta\mu_{H_2O} = -1.52$ eV) (b, d) $T = 550^\circ\text{C}$ and $P_{H_2O} = 0.3$ bar (FCC reactor entrance conditions; $\Delta\mu_{H_2O} = -1.05$ eV). The blue background range and yellow background range qualitatively specifies the range of ΔE_{NH_3} for weak silanol/aluminol sites and relatively stronger bridging/PBS sites, respectively.

Our findings suggest that achieving optimal Brønsted acidity requires a precise Si concentration, as excessive or insufficient Si incorporation can diminish the overall acid strength. However, because the surface of ASA is inherently heterogeneous, Figure 5c,d can be reinterpreted as the likelihood of forming structural ensembles that

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exhibit strong ΔE_{NH_3} and therefore Brønsted acidity. The probability of forming BAS or PBS increases with increasing Si coverage but diminishes as the surface becomes extensively covered with Si.

We also evaluated the Lewis acidity of Si-doped $\gamma\text{-Al}_2\text{O}_3$ using CO adsorption, as CO is more sensitive to weak Lewis acidity and, unlike NH_3 , does not migrate to nearby Brønsted acid sites. On the undoped (110) surface, strong Lewis acid sites are predominantly blocked by hydroxylation. However, under reaction conditions, certain metastable configurations with strong Lewis acidity can still emerge^[41]. A similar phenomenon occurs on Si-doped surfaces, but in these cases, silica strongly interacts with the Lewis acid-base pairs and water, effectively suppressing the surface's Lewis acidity.

In contrast, the undoped (001) surface becomes dehydroxylated under both reaction conditions, exposing undercoordinated Al^{V} atoms, which act as Lewis acid sites. Notably, silica adsorption does not entirely eliminate Lewis acidity on this surface, with a significant fraction of undercoordinated Al atoms remaining accessible (Figure S8 and Table S4). The number of strong Lewis acid sites on the (001) surface remains consistent across the Si coverage explored in our study.

Experimental Validation for Si/ Al_2O_3

Extensive prior literature on model silica-deposited alumina surfaces has established that an optimal Si/Al ratio or surface coverage exists that maximizes Brønsted acidity and, consequently, catalytic performance^[29,30]. These insights are directly echoed in the more recent study by Caillot et al.^[16], who examined *m*-xylene isomerization, a reaction highly sensitive to BAS, using model amorphous silica-alumina (ASA) synthesized via controlled grafting of Si species onto $\gamma\text{-Al}_2\text{O}_3$. Their work explored how the amount of grafted Si influenced catalytic performance. They observed that as Si deposition increased, the reaction rate rose significantly, highlighting the necessity of Si incorporation for creating BAS capable of catalyzing *m*-xylene isomerization. However, as Si coverage approached saturation, with the surface nearly fully covered, the rate of *m*-xylene isomerization declined, passing a maximum. This behavior aligns with our theoretical predictions which predict that the initial addition of Si promotes the formation of relatively strong BAS, however, excessive Si coverage leads to the formation of silanol groups, which are significantly less active. Furthermore, the turnover frequency (TOF) of *m*-xylene isomerization was 22 times lower than that observed over USY zeolite devoid of extra-framework aluminum. The reduced TOF is consistent with the lower ΔE_{NH_3} calculated for the BAS on Si-doped $\gamma\text{-Al}_2\text{O}_3$ compared to the stronger BAS found in zeolites, reinforcing that the Brønsted acidity of Si-doped $\gamma\text{-Al}_2\text{O}_3$ is stronger than that of pure $\gamma\text{-Al}_2\text{O}_3$ or SiO_2 , but remains considerably weaker than that of the bridging BAS in bulk zeolites.

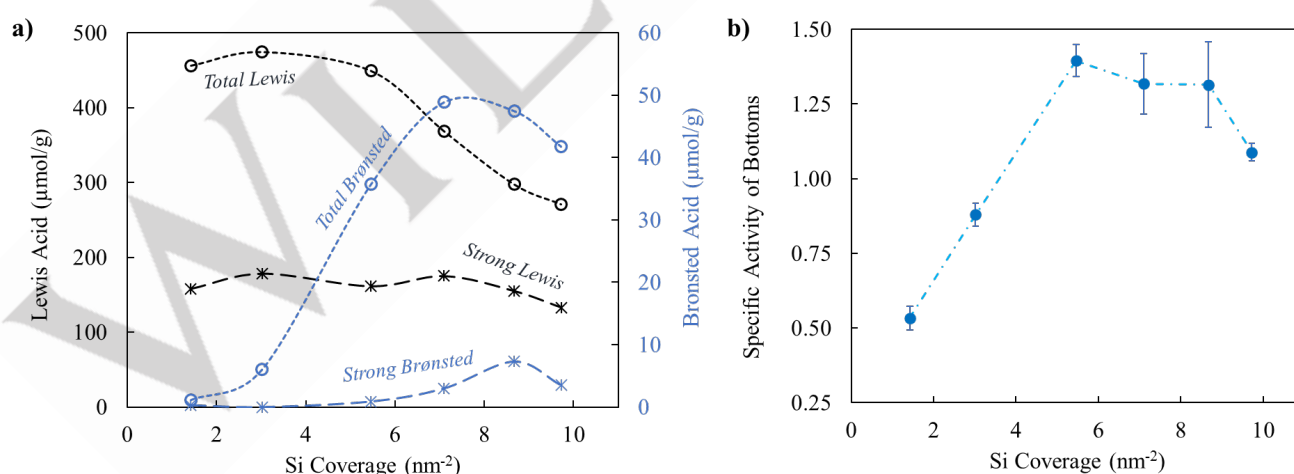


Figure 6: (a) The acid site concentration determined using adsorbed pyridine IR data is plotted with increasing silica surface coverage, calculated using steamed surface area. The total acid sites were determined after desorption at 453 K. The Strong acid sites were determined after desorption at 773 K. The Brønsted and Lewis acid were determined by bands at 1546 cm^{-1} and 1450 cm^{-1} , respectively. (b) The specific activity for bottoms cracking from the ACE unit^[54] is plotted with increasing silica weight %. The specific activity is the slope of $X/(1-X)^2$ vs (weight of catalyst to oil ratio), where X = bottoms conversion (Figure S13). Refer to the supporting information for detailed explanation. The error bars represent the one sigma standard deviation of the slopes of the activity plot (Figure S13).

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To investigate the impact of Si doping on the catalytic cracking of real FCC (Fluid Catalytic Cracking) feedstocks, we conducted experiments using an ACE™ unit^[54], a widely adopted fixed fluid bed reactor used throughout the refining industry. We synthesized Si-doped γ -Al₂O₃ samples with varying Si coverage and evaluated their catalytic performance. We would like to clarify that the samples have some amount of Na due to the synthesis process adopted. Previous computational studies, such as Digne et al.^[55], have shown that the migration of sodium cations into the γ -alumina bulk is energetically unfavorable. Instead, sodium cations preferentially exchange with protons belonging to HO- μ_3 groups, which may lead to a decrease in Brønsted acidity observed in many experiments. Therefore, we acknowledge there is possibility that some Brønsted acidity is poisoned by sodium in the industrial catalyst. In the supporting information we provide details of sodium cations exchange energy and its correlation with ammonia binding energy (Figure S11).

Pyridine adsorption followed by FTIR spectroscopy was employed to quantify the Brønsted acid site density on each sample. The density of total BAS increased with increasing Si coverage (Table S6), reaching a maximum at around 9 Si nm⁻². The strong BAS, as identified by their stability during N₂ purging at higher temperatures (773 K), are observed only near the maximum total BAS density. However, our calculations reveal an ensemble of strong acid sites with varying strengths, some of which do not exhibit proton transfer. This variability implies that characterization techniques, such as pyridine FTIR spectroscopy, may not fully capture the complete population of acid sites as the BAS characterized by pyridinium ion formation. In contrast, the density of strong Lewis acid sites remain constant across the range of Si coverages studied. This indicates that while Brønsted acidity is highly sensitive to Si incorporation and synthesis conditions, strong Lewis acidity is largely unaffected. Overall, the experimental trends align qualitatively with our theoretical predictions. Nonetheless, we would like to emphasize that pyridine FTIR is inherently limited in its ability to distinguish between different types of Brønsted acid sites^[56]. Advanced solid-state NMR techniques could potentially resolve these distinctions more clearly, though such analyses are beyond the scope of the present study.

Figure 6b presents the catalytic activity trends as a function of SiO₂ content. The catalyst exhibits optimum activity at 4.5 nm⁻² or 6.8 wt % SiO₂, which is lower than the previous studies by Caillot et al.^[16] (~17 wt % SiO₂ for m-xylene isomerization) and Sato et al.^[30] (~12 wt % SiO₂ for 1-isobutene isomerization). We attribute this lower optimum to two key factors - reaction specificity and thermal pretreatment. Our feed is a gas-oil mixture containing substantially larger molecules than 1-isobutene or m-xylene. Additionally, all samples were pre-steamed at 732°C for 17 h in 100 % steam, then post-steamed at 871°C for 4 h. These higher temperatures likely drive the material toward thermodynamic equilibrium structures, closely resembling those sampled in our computational study and favoring lower silica loadings. Nevertheless, the data clearly show that Si incorporation plays a critical role in enhancing catalytic activity for FCC, with a strong correlation observed between activity and the population of Brønsted acid sites (BAS). This highlights the significance of optimizing Si content to maximize BAS density and, consequently, catalytic performance.

Conclusion

In this study, we present a comprehensive analysis of amorphous silica-alumina surfaces using well-defined Si/ γ -Al₂O₃ surfaces, elucidating the structural evolution and acid-site formation mechanisms crucial for catalytic applications. Density functional theory calculations on the (001) and (110) surfaces reveal that initial Si deposition is energetically favored on the (001) surface. However, as Si coverage increases, both surfaces contribute to Brønsted acid site formation. Furthermore, we propose that high-temperature pretreatment may induce Si migration from the (001) to the (110) surface.

By developing MLIPs to accelerate the energy calculations and sampling methods to efficiently explore surface configurations, we address the long-standing debate regarding the precise structure of the relatively strong Brønsted acid sites by demonstrating that acidity on Si/ γ -Al₂O₃ arises from an ensemble of active sites with comparable acidity, as probed by NH₃ binding energy. This dynamic view of Brønsted acidity, conceptualized as a spectrum rather than discrete categories, provides a more nuanced understanding of the catalytic properties. The results indicate that Brønsted acidity is not localized to a single, well-defined site but instead emerges from a heterogeneous distribution of structurally diverse sites.

Framing Brønsted acidity as a spectrum of structurally distinct but energetically overlapping sites offers a fresh perspective on why decades of spectroscopy have struggled to assign one “dominant” acid site. Our ensemble picture helps reconcile apparently conflicting IR, NMR, and adsorption data and provides concrete structural targets, ranked by probability, that can guide the design of future experiments.

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Our findings reveal that the (110) surface, due to its higher intrinsic Lewis acidity, promotes the structural rearrangements necessary for Si-O-Al chain formation, thereby enhancing Brønsted acidity. In contrast, the (001) surface exhibits weaker acidity at lower Si coverages and requires higher hydroxylation levels to achieve effective BAS formation. This distinction aligns with experimental observations, which demonstrate a correlation between increased Si incorporation and enhanced catalytic activity, particularly in reactions like m-xylene isomerization^[16] or cracking of 1,3,5-triisopropylbenzene^[15].

We further demonstrate that optimal acidity occurs at intermediate Si coverages. At these levels, the formation of strong BAS is maximized, whereas excessive Si coverage leads to a decline in acid sites due to the predominance of weakly acidic silanol groups. These results highlight the importance of maintaining a critical balance in Si doping to enhance catalytic performance, emphasizing that surface heterogeneity and controlled Si incorporation are key factors in developing highly effective catalysts. The test of the Si/ γ -Al₂O₃ catalyst with cracking gas-oil feed confirmed that the inclusion of Si improves the activity for hydrocarbon cracking.

In conclusion, the study advances the understanding of amorphous aluminosilicates by providing atomistic insights into the structural factors that affect Brønsted acid-site formation. These findings have significant implications for catalyst design, offering guidance for optimizing acidity to enhance performance in industrial processes such as catalytic cracking.

Supporting Information

The authors have cited additional references within the Supporting Information.

Acknowledgements

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Keywords: Amorphous Silica-Alumina • Fluidized Catalytic Cracking • Brønsted Acidity • Lewis Acidity • Acid Structure

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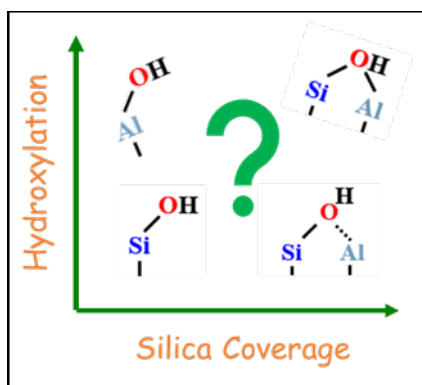
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Entry for the Table of Contents



Amorphous silica-alumina plays a key role in Fluid Catalytic Cracking (FCC), but its active sites are hard to define due to atomic disorder. Here, we analyze its structure-acidity relationship under FCC conditions and observe that diverse acid sites emerge, including zeolite-like and pseudo-bridging Brønsted sites, influenced by Si content and hydroxylation. Using theory and experiments we confirm Brønsted acidity peaks at an optimal Si coverage.