

Pseudo-bridging Silanols as Versatile Brønsted Acid Sites of Amorphous Aluminosilicates Surfaces

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Introduction

Unraveling the surface structure of amorphous silica-alumina (ASA) is a main challenge in the literature of materials chemistry and catalysis. The existence of zeolite-like Si-(OH)-Al groups (Fig. 1a) as Brønsted acid sites is strongly debated. Silanols in the vicinity of aluminum atoms are also invoked (Fig. 1b). Trombetta et al.[1] suggest that such sites could bridge with Al atoms after adsorption of a nitrogenated probe molecule (Fig. 1c), which has been contradicted in the case of CO adsorption by Crépeau et al.[2] We propose the first ASA surface model, by simulating the amorphization process occurring upon contacting silica derivatives with the γ -Al₂O₃ surface. We study the stability of the ASA phase and the nature of Brønsted and Lewis acid sites as a function of the temperature and the water pressure. Assignment of FTIR spectra is provided, as well as an atomistic insight in the adsorption of probe molecules (CO, Pyridine, Lutidine, NH₃).

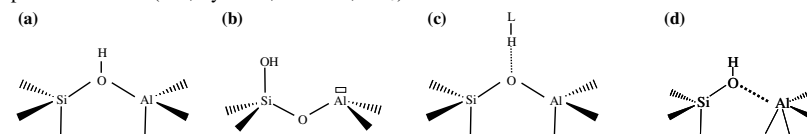


Figure 1. Structure of surface Brønsted acid sites of ASA debated in the literature: (a) Bridging OH group, (b) Silanol in the vicinity of Al,[2] (c) Bridging upon adsorption of a probe molecule L.[1]. (d) Pseudo-bridging Silanols (PBS) simulated in the present work.

Methods

Periodic Density Functional Theory (DFT, GGA-PW91) geometry optimization and vibrational analysis are performed with the VASP 4.6. code. Force-field NVT molecular dynamics are performed with the GULP program (Catlow potentials, time step 1fs, simulation time 30 ps). A simulated annealing sequence consists in: (i) DFT geometry optimization, (ii) force-field molecular dynamics at 1023 K, (iii) DFT quenching of stable states identified by (ii).

Results and Discussion

Exchange of surface OH groups of γ -Al₂O₃ (100) (model from [3]) with Si(OH)₄ is simulated to reproduce the surface structure of ASA samples obtained from organosilane deposition on alumina followed by hydrolysis. Without any thermal treatment, our calculations demonstrate that silica aggregates are formed, in weak contact with γ -Al₂O₃, only by few anchoring points. Stabilization and phase transition is provided upon further thermal treatment (modeled by the simulated annealing sequence). An ASA phase forms, revealing some original Lewis acid sites thanks to extraction of Al atoms from the alumina surface to the ASA phase (Fig. 2a). Hydroxylation of the ASA surface is studied as a function of the temperature and the water pressure (Fig. 2b). Original Brønsted acid sites are revealed (Fig. 1d) and called Pseudo-

Bridging Silanols (PBS). A small amount of bridging Si-(OH)-Al groups is also modeled. The calculation of stretching frequencies of OH groups allows the validation of the proposed hydroxylated surface obtained from this model. The interaction of PBS with basic probe molecules (Fig. 2c) can lead to their full bridging with the Al atom in the case of nitrogenated molecules of increasing basic strength, as inferred by Trombetta et al.[1] (Fig. 1c) but not upon CO adsorption, in line with the observations of Crépeau et al.[2]. The behavior of PBS thus strongly depends on the nature of the probe molecule, for what concerns deprotonation but also for the formation of new surface O-Al bonds. This bridging ability is shown to depend on the Si-O...Al angle. Our simulations moreover suggest that partial demixing of the ASA phase can be expected at high water pressure (Fig. 2b).

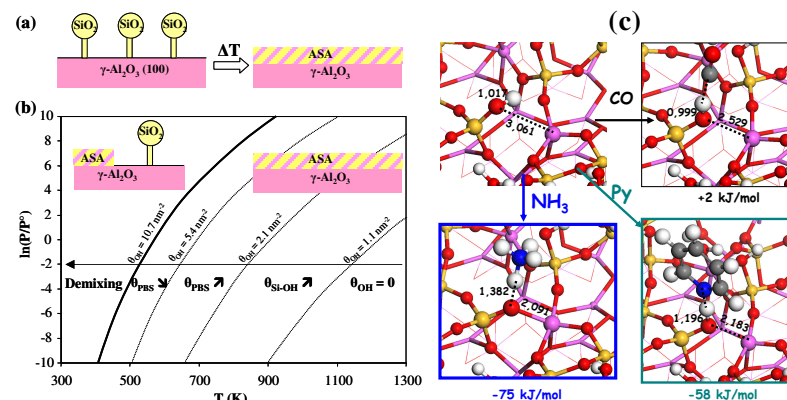


Figure 2. (a) Formation of an ASA phase upon thermal treatment of grafted silica on γ -Al₂O₃ (100) ($\theta_{Si} = 6.4 \text{ nm}^{-2}$). (b) Further behavior upon water exposure as a function of T and P_{H_2O} . (c) Behavior of PBS sites for $\theta_{OH} = 5.4 \text{ nm}^{-2}$, upon CO, Pyridine and NH₃ adsorption.

Significance

ASA are widespread supports for multifunctional heterogeneous catalysts in fine chemistry, petrochemical and refining, from the laboratory scale to the industrial plant. These materials are also suspected to be H-USY zeolites.[4] The present work provides unedited clues for the resolution of their debated structure as well as for their stability, reactivity and for the link between the local structure of surface sites and their acidity.

References

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