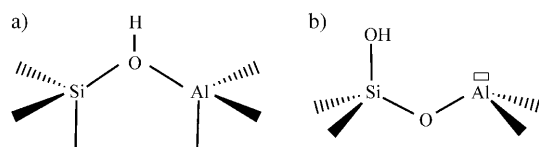


Pseudo-Bridging Silanols as Versatile Brønsted Acid Sites of Amorphous Aluminosilicate Surfaces**

Céline Chizallet* and Pascal Raybaud

Unraveling the surface structure of amorphous silica–alumina (ASA) is a main challenge in materials chemistry and catalysis, despite improvement thanks to magic-angle spinning NMR spectroscopy.^[1,2] Taking advantage of their combined Lewis and Brønsted acidities, these materials are widely used as supports for multifunctional heterogeneous catalysts in fine chemistry,^[3–7] petrochemistry, and refining,^[8–10] and they raise the fundamental question of the link between the local structure of surface sites and their acidity. The existence of zeolite-like Si–(OH)–Al groups is strongly debated. Silanols in the vicinity of aluminum atoms^[11,12] are also invoked (Scheme 1). Molecular modeling studies have recently provided relevant insights in the atomic structure and reactivity of acid sites of crystalline networks.^[13–16] However, to our knowledge, modeling of the acidity revealed by amorphous surfaces has never been undertaken.



Scheme 1. Structure of Brønsted acid sites of ASA proposed in the literature: a) Bridging OH group, b) Silanol in the vicinity of Al.^[11]

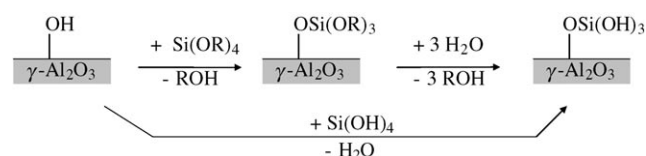
Herein we propose the first ASA surface model, by simulating the contact of silica derivatives with the γ -Al₂O₃ (100) surface. We show that this poorly reactive alumina surface develops a strong tendency to amorphization upon interaction with silica, and reveals some original Lewis and Brønsted acid sites thanks to the formation of an ASA phase, in the limit of demixing at high water pressure. Periodic DFT calculations and force-field molecular dynamics were used to study the effect of thermal treatments. The γ -Al₂O₃ (100) surface model established previously^[17] was used as starting configuration, and larger unit cells (ca. 500 atoms) were considered to allow for the amorphization process within a periodic model.

[*] Dr. C. Chizallet, Dr. P. Raybaud
Direction Catalyse et Séparation, IFP-Lyon
BP3, 69360 Solaize (France)
Fax: (+33) 4-7802-2066
E-mail: celine.chizallet@ifp.fr

[**] We thank H. Toulhoat, A. Chaumonnot, M. Digne, and F. Bertoncini from IFP for fruitful discussions.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.200804580>.

Deposition of organosilanes on γ -Al₂O₃ yields silicated alumina with satisfactory control of the amount of deposited silica.^[18] An exchange process with OH groups of alumina takes place (through a condensation reaction with organosilane molecules),^[19–21] followed by hydrolysis (Scheme 2), which is formally equivalent to silicic acid Si(OH)₄ exchange with γ -Al₂O₃ OH groups, quantified by the exchange energy $\Delta_{\text{exch}} U$.



Scheme 2. Organosilane monodentate deposition and hydrolysis on γ -Al₂O₃.

We determined by DFT the Si(OH)₄ exchange ability of the fully hydrated γ -Al₂O₃ (100) surface ($\theta_{\text{OH}} = 17.1 \text{ nm}^{-2}$), which exhibits molecularly adsorbed water molecules, μ_1 -OH and μ_3 -OH. A systematic study for a Si(OH)₄ coverage $\theta_{\text{Si}} = 0.5 \text{ nm}^{-2}$ of the preferred exchanged configurations leads to the competitive bidentate (exchange with μ_1 -OH and μ_3 -OH, $\Delta_{\text{exch}} U = -29 \text{ kJ mol}^{-1}$) and monodentate (exchange with μ_1 -OH, $\Delta_{\text{exch}} U = -23 \text{ kJ mol}^{-1}$) structures depicted in Figure 1 a–c, which is in agreement with IR spectroscopic evidence of exchange mainly with μ_1 -OH.^[21]

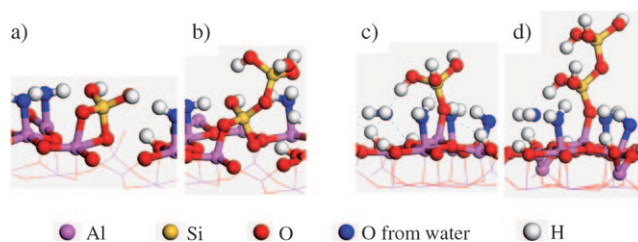


Figure 1. Preferred exchanged structures, calculated by DFT, of Si(OH)₄ on γ -Al₂O₃ (100): a) bidentate, $\theta_{\text{Si}} = 0.5 \text{ Si nm}^{-2}$, b) ex-bidentate, $\theta_{\text{Si}} = 1.1 \text{ Si nm}^{-2}$, c) monodentate, $\theta_{\text{Si}} = 0.5 \text{ Si nm}^{-2}$, d) ex-monodentate, $\theta_{\text{Si}} = 1.1 \text{ Si nm}^{-2}$.

The second Si(OH)₄ molecule ($\theta_{\text{Si}} = 1.1 \text{ nm}^{-2}$) condenses with the previously grafted species (Figure 1 b–d), instead of grafting on another alumina site. The condensation reaction energies (-37 and -29 kJ mol^{-1}), typical of gas-phase condensation of Si(OH)₄ (-21 kJ mol^{-1}), show that increasing the silicic acid content in a wet environment will undoubtedly lead to the growth of silica particles in weak contact with γ -Al₂O₃ (100), only by few anchoring points. Without any thermal treatment, no intimate interaction between silica and γ -Al₂O₃ exists through the (100) orientation.

We thus investigated the effect of thermal treatment for $\theta_{\text{Si}} = 6.4 \text{ nm}^{-2}$. To reach quickly a thermodynamically stable state, we started from an epitaxially deposited silica film over the $\gamma\text{-Al}_2\text{O}_3$ dehydrated surface (see Figure S1 in the Supporting Information), further submitted to the simulated annealing sequence at 1023 K described in the Methods Section. The most stable surface found (Figure 2a) reveals an ASA surface phase, formed by extraction of Al atoms (III_i and II_i) from $\gamma\text{-Al}_2\text{O}_3$ (100). These results unravel the determining role of thermal treatments in the activation of the formation of an ASA phase, as shown in schematic form in Figure 3a. The extracted Al atoms, issued from bulk Al_{VI} , are finally either Al_{V} (II_i , III_3) or Al_{IV} (III_1 , III_2 , III_4) (see Figure S1.2 in the Supporting Information). This trend is fully in line with the experimental ^{27}Al NMR observation of the higher $\text{Al}_{\text{IV}}/\text{Al}_{\text{VI}}$ ratio in ASA than in $\gamma\text{-Al}_2\text{O}_3$,^[11,22,23] and of the appearance of new Al_{V} species.^[23,24] In the literature, silicic 2MR species were invoked on highly dehydrated amorphous silica:^[25,26] one silicic two-membered ring 2MR ($\text{Si}(\text{X}_2)\text{--Si}(\text{Y}_2)$) and one Si–Al 2MR ($\text{Si}(\text{W}_1)\text{--Al}(\text{III}_1)$) are also present on our surface model.

The behavior of this ASA surface phase towards increasing amounts of water, by molecular adsorption on M atoms ($\text{M} = \text{Al}, \text{Si}$), dissociation by $\text{M}\text{--O}$ pairs, and hydrolysis of $\text{M}^1\text{--O--M}^2$ bridges, was then considered by DFT calculations. An additional process, which we call “shifted hydrolysis”, was revealed, which takes place at the surrounding of Si–O–Al fragments. It formally consists of their hydrolysis, producing two silanol groups but no Al–OH groups (Scheme 3). The first water molecule added in the unit cell (1.1 OH nm^{-2}) hydrolyzes the silicic 2MR species with a hydration energy $\Delta_{\text{hyd}}U = -249 \text{ kJ mol}^{-1}$. For a coverage from 2.1 to 4.3 OH nm^{-2} , shifted hydrolysis is the favored process with $-211 \leq \Delta_{\text{hyd}}U \leq -135 \text{ kJ mol}^{-1}$. Hence, until a coverage of 4.3 OH nm^{-2} , only silanol groups are formed, which explains why a band at 3740 cm^{-1} dominates the IR spectra of silicated alumina.^[11,27]

One silanol group obtained upon shifted hydrolysis keeps interacting with the neighboring Al atom (Scheme 3). This OH group can thus be defined as a “pseudo-bridging silanol” (PBS). PBSs are suspected to be relevant sites for the milder acidity of ASA compared with zeolites. They also rationalize the versatility of the experimentally measured acid strengths on ASA samples,^[11,27] as the flexibility afforded by pseudo-bridging provides a distribution of Si–O–Al angles and Al–O distances (see Figure S2-1 and Table S2-1 in the Supporting Information), whereas they are fixed by the lattice properties in a zeolite. Moreover, the coordination number of the Al acceptor atom, either 4 or 5, also tunes the acidity of the PBS. Some PBS species emphasized in Figure 2b also correspond

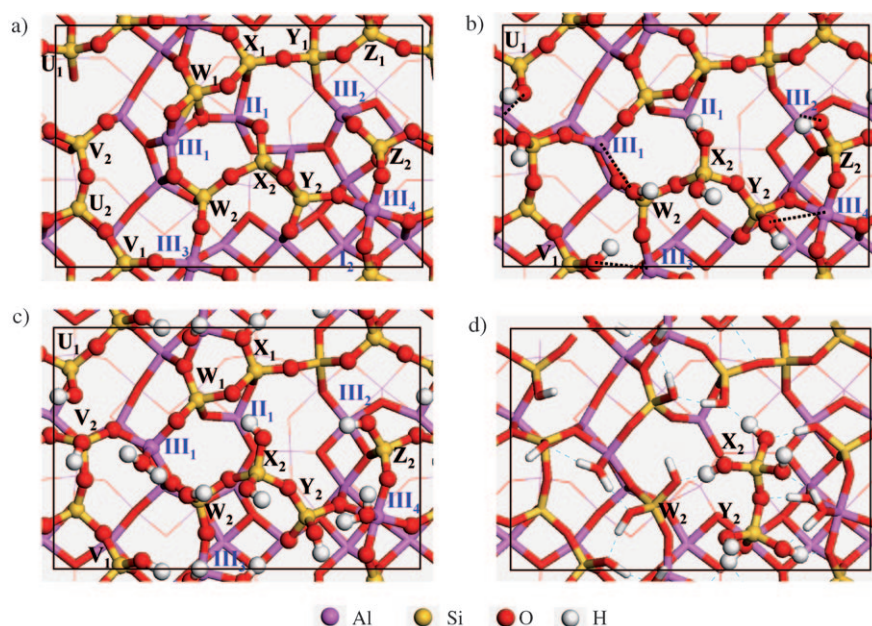


Figure 2. Top views (balls represent outermost atoms) of simulated systems obtained upon epitaxial deposition of a silica film ($\theta_{\text{Si}} = 6.4 \text{ Si nm}^{-2}$) on $\gamma\text{-Al}_2\text{O}_3$ (100): a) geometry after simulated annealing ($\theta_{\text{OH}} = 0 \text{ nm}^{-2}$); b) hydrated geometry at $\theta_{\text{OH}} = 4.3 \text{ nm}^{-2}$; PBS sites are depicted by dotted lines; c) $\theta_{\text{OH}} = 7.5 \text{ nm}^{-2}$; and d) $\theta_{\text{OH}} = 10.7 \text{ nm}^{-2}$.

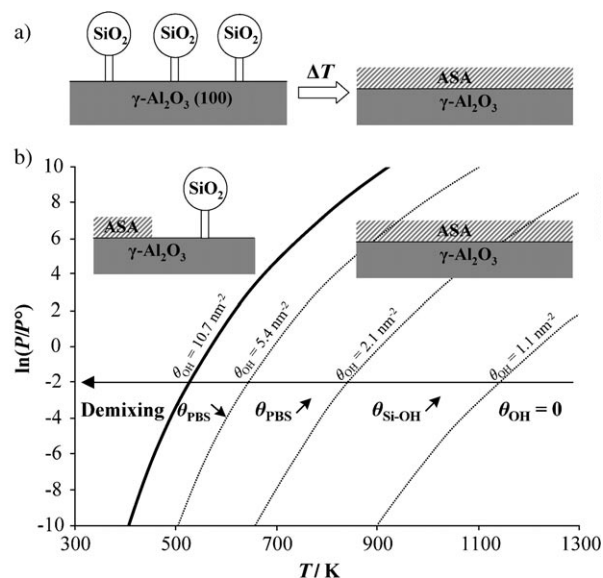
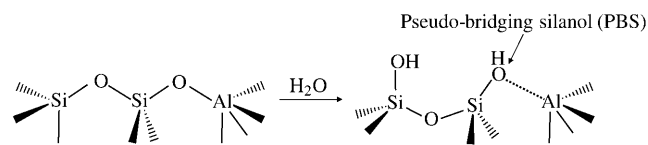


Figure 3. a) Formation of an ASA phase upon thermal treatment of grafted silica aggregates on $\gamma\text{-Al}_2\text{O}_3$ (100) for $\theta_{\text{Si}} = 6.4 \text{ nm}^{-2}$. b) Further behavior upon water exposure as a function of temperature and water partial pressure.



Scheme 3. Shifted hydrolysis process of Si–O–Al bridges.

to the definition of silanols in Scheme 1b,^[11] because of covalent Si–O–Al bridges (silanols hold by U₁, Y₂, W₂, Z₂) with the restriction that Al_{III} cannot exist in wet environment.

For $\theta_{\text{OH}} = 5.4$ to 9.6 nm^{-2} , hydrolysis of siloxane and Si–O–Al bridges and molecular adsorption of water on Al_{IV} occur with values of $-128 \leq \Delta_{\text{hyd}}U \leq -80 \text{ kJ mol}^{-1}$. The latter process leads to gradual conversion of PBSs into nonbridging silanols with the saturation of PBS acceptors Al atoms by water. One bridging Si(X₁)–OH–Al(III₃) group is also obtained (Figure 2c), which could correspond to the few sites exhibiting a zeolite-like activity.^[28] Its moderate stability ($\Delta_{\text{hyd}}U = -97 \text{ kJ mol}^{-1}$ only), in contrast to structural OH groups of zeolites, is a rational explanation of the ¹H NMR signal at $\delta = 5\text{--}7$ ppm only for low-temperature pretreated samples.^[22,29,30] At $\theta_{\text{OH}} = 10.7 \text{ nm}^{-2}$ (Figure 2d), hydrolysis of a siloxane bridge induces the release of one {Si(OH)₃}₂ dimer (X₂ and Y₂): beyond this θ_{OH} value, water segregates a fraction of the silica from the ASA phase.

For a given water pressure, the temperature window maximizing the amount of PBS is quite narrow (ca. 200 K, Figure 3b): to obtain tuned acidity, the pretreatment temperature and atmosphere have to be chosen carefully.

In summary, we propose the first surface model of ASA, providing evidence for the need of thermal treatment after the deposition of silica to reach the mixed phase, by Al extraction from the alumina support. This surface is likely to exhibit pseudo-bridging silanols (PBSs) and only a few zeolite-like bridging OH groups. Partial demixing of the ASA phase occurs upon further water adsorption.

Methods

DFT calculations, in the framework of the GGA-PW91 functional,^[31] were performed with the VASP 4.6 code.^[32] The interaction between core and valence electrons was described by the projector augmented waves (PAW) approach^[33] with an energy cutoff of 265 eV.

Force-field NVT molecular dynamics calculations were performed with the GULP program^[34] using Catlow potentials.^[35,36] A time step of 1 fs was used for a total simulation time of 30 ps. The simulated annealing sequence was: 1) DFT geometry optimization, 2) force-field molecular dynamics at 1023 K, 3) DFT quenching of stable states identified by step 2 (see S3 in the Supporting Information for details).

Thermodynamic stability domains were drawn as a function of the temperature T and the water partial pressure P by writing the surface energy systems according to Equation (1). S° and H° are the standard entropy and enthalpy of the water molecule.

$$\Gamma(T) = \Gamma_{(0\text{K})} + \frac{\gamma_{\text{OH}}}{2} \left[T S_{(T)}^\circ - H_{(T)}^\circ + S_{(0\text{K})}^\circ - k T \ln \left(\frac{P}{P^\circ} \right) \right] \quad (1)$$

Received: September 17, 2008

Revised: December 9, 2008

Published online: January 19, 2009

Keywords: acidity · aluminosilicates · density functional calculations · surface chemistry · water adsorption

- [1] A. Omegna, J. A. van Bokhoven, R. Prins, *J. Phys. Chem. B* **2003**, *107*, 8854.
- [2] J. F. Stebbins, Z. Xu, *Nature* **1997**, *390*, 60.
- [3] V. Dufaud, J. M. Basset, *Angew. Chem.* **1998**, *110*, 848; *Angew. Chem. Int. Ed.* **1998**, *37*, 806.
- [4] M. Jezequel et al., *J. Am. Chem. Soc.* **2001**, *123*, 3520.
- [5] A. W. Moses, C. Raab, A. E. Nelson, H. D. Leifeste, N. A. Ramsahye, S. Chattopadhyay, J. Eckert, B. F. Chmelka, S. L. Scott, *J. Am. Chem. Soc.* **2007**, *129*, 8912.
- [6] K. Motokura, M. Tada, Y. Iwasawa, *J. Am. Chem. Soc.* **2007**, *129*, 9540.
- [7] C. Thieuleux, A. Maraval, L. Veyre, C. Cop  ret, D. Soulivong, J. M. Basset, G. J. Sunley, *Angew. Chem.* **2007**, *119*, 2338; *Angew. Chem. Int. Ed.* **2007**, *46*, 2288.
- [8] A. Corma, *Chem. Rev.* **1995**, *95*, 559.
- [9] C. Marcilly, *Acido-Basic Catalysis*, Technip, Paris, **2005**.
- [10] G. Busca, *Chem. Rev.* **2007**, *107*, 5366.
- [11] G. Cr  peau, V. Montouillout, A. Vimont, L. Marier, T. Cseri, F. Maug  , *J. Phys. Chem. B* **2006**, *110*, 15172.
- [12] M. Trombetta, G. Busca, S. Rossini, V. Piccoli, U. Cornaro, A. Guercio, R. Catani, R. J. Willey, *J. Catal.* **1998**, *179*, 581.
- [13] R. A. van Santen, M. Neurock, *Molecular Heterogeneous Catalysis*, Wiley-VCH, Weinheim, **2006**.
- [14] C. Tuma, J. Sauer, *Angew. Chem.* **2005**, *117*, 4847; *Angew. Chem. Int. Ed.* **2005**, *44*, 4769.
- [15] J. Hafner, L. Benco, T. Bucko, *Top. Catal.* **2006**, *37*, 41.
- [16] M. Digne, P. Raybaud, P. Sautet, D. Guillaume, H. Toulhoat, *J. Am. Chem. Soc.* **2008**, *130*, 11030.
- [17] M. Digne, P. Sautet, P. Raybaud, P. Euzen, H. Toulhoat, *J. Catal.* **2002**, *211*, 1.
- [18] N. Katada, M. Niwa, *Chem. Vap. Deposition* **1996**, *2*, 125.
- [19] J. D. Alexander, A. N. Gent, P. N. Henriksen, *J. Chem. Phys.* **1985**, *83*, 5981.
- [20] M. Lindblad, A. Root, *Stud. Surf. Sci. Catal.* **1998**, *118*, 817.
- [21] P. Sarrazin, S. Kasztelan, N. Zanier-Szydlowski, J. P. Bonnelle, J. Grimblot, *J. Phys. Chem.* **1993**, *97*, 5947.
- [22] C. Dor  mieux-Morin, C. Martin, J. M. Br  geault, J. Fraissard, *Appl. Catal.* **1991**, *77*, 149.
- [23] B. M. De Witte, P. J. Grobet, J. B. Uytterhoeven, *J. Phys. Chem.* **1995**, *99*, 6961.
- [24] J. P. Gilson, G. C. Edwards, A. W. Peters, K. Rajagopalan, R. F. Wormsbecher, T. G. Roberie, M. P. Shatlock, *J. Chem. Soc. Chem. Commun.* **1987**, 91.
- [25] B. A. Morrow, I. A. Cody, *J. Phys. Chem.* **1976**, *80*, 1995.
- [26] B. C. Bunker, D. M. Haaland, K. J. Ward, T. A. Michalske, W. L. Smith, J. S. Binkley, C. F. Melius, C. A. Balfe, *Surf. Sci.* **1989**, *210*, 406.
- [27] W. Daniell, U. Schubert, R. Gl  ckler, A. Meyer, K. Noweck, H. Kn  zinger, *Appl. Catal. A* **2000**, *196*, 247.
- [28] B. Xu, C. Sievers, J. A. Lercher, J. A. R. van Veen, P. Giltay, R. Prins, J. A. van Bokhoven, *J. Phys. Chem. C* **2007**, *111*, 12075.
- [29] C. E. Bronnimann, I. S. Chuang, B. L. Hawkins, G. E. Maciel, *J. Am. Chem. Soc.* **1987**, *109*, 1562.
- [30] M. Hunger, D. Freunde, H. Pfeifer, H. Bremer, M. Jank, K. P. Wendlandt, *Chem. Phys. Lett.* **1983**, *100*, 29.
- [31] J. Perdew, Y. Wang, *Phys. Rev. B* **1992**, *45*, 13244.
- [32] G. Kresse, J. Hafner, *Phys. Rev. B* **1994**, *49*, 14251.
- [33] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758.
- [34] J. D. Gale, *Philos. Mag.* **1996**, *73*, 3; J. D. Gale, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 629.
- [35] K. P. Schr  der, J. Sauer, M. Leslie, C. R. A. Catlow, J. M. Thomas, *Chem. Phys. Lett.* **1992**, *188*, 320.
- [36] J. D. Gale, N. J. Henson, *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 3175.