Reactivity of shape-controlled crystals and metadynamics simulations locate the weak spots of alumina in water

R. Réocreux, É. Girel, P. Clabaut, A. Tuel, M. Besson, A. Chaumonnot, A. Cabiac, P. Sautet & C. Michel

The kinetic stability of any material in water relies on the presence of surface weak spots responsible for chemical weathering by hydrolysis. Being able to identify the atomistic nature of these sites and the first steps of transformation is therefore critical to master the decomposition processes. This is the challenge that we tackle here: combining experimental and modeling studies we investigate the stability of alumina in water. Exploring the reactivity of shape-controlled crystals, we identify experimentally a specific facet as the location of the weak spots. Using biased ab initio molecular dynamics, we recognize this weak spot as a surface exposed tetra-coordinated Al atom and further provide a detailed mechanism of the first steps of hydrolysis. This understanding is of great importance to heterogeneous catalysis where alumina is a major support. Furthermore, it paves the way to atomistic understanding of interfacial reactions, at the crossroad of a variety of fields of research.
The kinetic stability of solids in water is governed by their reactivity at the interface. Being able to understand and control their surface stability and desired properties is therefore at the heart of a variety of research fields: kinetics of drug release, corrosion of metals and alloys, lithium batteries, geochemistry with in particular the re-equilibration of solid phases in presence of a liquid, water treatment, heterogeneous catalysis, from the preparation, the utilization to the chemical composition: silica deposition, presence of metallic geochemistry with in particular the re-equilibration of solid phase conditions.

It is only recently that Ngouana-Wakou drug release, corrosion of metals and alloys, lithium batteries, phases in presence of a liquid, water treatment, heterogeneous catalysis involving bonds with a partial covalent character (typically here Al–O and O–H bonds) hence requiring an ab initio description.

Here, we combine experiments and theory to provide the relative affinity of water for the different facets and the inhibiting coverage of polyol at which the decomposition of alumina gets inhibited, that is no hydroxides can be detected by XRD after hydrothermal treatment (see Supplementary Note 2). This quantification of polyol at which the decomposition of alumina gets inhibited, is that no hydroxides can be detected by XRD after hydrothermal treatment (see Supplementary Note 2). This quantity, referred to as inhibiting coverage, is reached for concentrations of 4 g L⁻¹ of polyols for 2 g of alumina in 50 mL of solution and varies from 0.15 to 0.30 nm⁻² for xylitol, and from 0.20 to 0.35 nm⁻² for sorbitol, depending on the shape of the nanoparticles (see Supplementary Table 4). This strong variation of the inhibiting coverage with the distribution of facet surface areas (up to a factor of two in the case of xylitol) indicates that each facet does not interact equally with the two polyols.

In the case of a specific adsorption on one facet only, the so-determined inhibiting coverage increases linearly with the fractional surface area of this facet with a zero-intercept (see Supplementary Note 4). As shown in Fig. 1d–f, this is only with the fractional surface area of the hydrophilic (110) facet that the inhibiting coverage of both sorbitol and xylitol correlates with a zero-intercept function. We cannot establish such correlations with the other fractional surface areas. Following the same kind of reasoning, we show in Supplementary Note 5 that edges and kinks are unlikely to be involved as major active sites for hydrolysis. Therefore, the adsorption of sorbitol or xylitol is specific to the (110) facet and allows for the total inhibition of the decomposition of γ-Al₂O₃ in liquid water at similar partial coverage of 0.36 and 0.44 nm⁻² of (110) facet for xylitol and sorbitol, respectively (slopes on Fig. 1d). As a corollary, we can infer that the (110) facet must exhibit sites responsible for the hydrolysis of γ-Al₂O₃ and that the reactivity of these sites with water can be limited or even suppressed upon the adsorption of sorbitol or xylitol.
Identification of the atomic sites on the (110) facet whence the decomposition initiates. To gain atomistic insight and identify the sites involved in the decomposition of $\gamma$-Al$_2$O$_3$ on the (110) facet, we have performed ab initio simulations using our recently developed model for $\gamma$-Al$_2$O$_3$/water interfaces. The primitive cell of the model of the $\gamma$-Al$_2$O$_3$(110) surface shows four different surface Al sites: two octahedral and two tetrahedral sites, referred to as Al$_{111}$ and Al$_{112}$ for the former and Al$_{11}$ and Al$_{12}$ for the latter (see Fig. 2a, b). This surface is fully hydrated with five chemisorbed water fragments, the oxygen atoms of which are represented in blue in Fig. 2a, b. Some of these water molecules are dissociated, generating hydroxyl surface groups. Repeating the surface unit cell in the x and y directions, the resulting p(2 × 2) slab is surmounted by a 20 Å thick layer of liquid water that is not represented here for clarity. The iso-electric point of alumina being close to 8, we consider pure neutral water. Since the decomposition of $\gamma$-Al$_2$O$_3$ transforms tetrahedral Al sites into octahedral Al centers, we have focused on the tetrahedral sites, Al$_a$ and Al$_b$, and their reactivity with water (see Fig. 2a). Both of them have a coordination number to alumina oxygen atoms (CN$_a$) of three and a coordination number to water oxygen atoms (CN$_w$) of one. Performing ab initio metadynamics, we have made each tetrahedral Al center specifically react along these two variables (see details in Methods). The statistical analysis of the variations of CN$_w$ and CN$_a$ allows for the construction of free energy landscapes (like the one given in Fig. 2c), the local depth of which assesses for the stability of the intermediates, transition states and products encountered along the course of the simulation (see details in Supplementary Note 6). Obtaining this mechanistic information is a key achievement in the quest of a better understanding of reactive interfaces and kinetic stability of solids in water. In the case of Al$_a$, the free energy landscape mainly shows one deep minimum at (CN$_a$,CN$_w$) = (3,1), that is the initial structure (see Supplementary Fig. 6). Even within a span of 200 kJ mol$^{-1}$, no transition state to escape that deep well towards other minima has been identified. This suggests that Al$_a$ is very unlikely to react with liquid water. Conversely, the free energy landscape for Al$_b$ shows, over a span of 180 kJ mol$^{-1}$, a variety of minima spread over the nodes of a well-defined checkered pattern and associated with a decreased number of bonds to alumina surface oxygen atoms and increased number with water oxygens (see Fig. 2c). Al$_b$ therefore progressively detaches from the oxygen network of $\gamma$-Al$_2$O$_3$ and is hydrated with the surrounding water molecules. A more detailed look at the free energy surface indicates that this hydration is sequential and follows an addition/elimination mechanism. It is only when Al$_b$ has reached a total coordination number of 5 that an Al$_b$–O–Al bond cleavage occurs. Noticeably, five-coordinated species appear to be key intermediates in the decomposition of alumina as in the water-induced de-alumination of zeolites. This holds true until (CN$_a$,CN$_w$) = (1,4) where Al$_b$ readily guests a water molecule to achieve an octahedral structure with (CN$_a$, CN$_w$) = (1,5). This last structure obtained from the simulation is represented in Fig. 2e and shows how Al$_b$ has been extracted from its initial position. Among the water molecules in the first coordination sphere, three of them were initially present on the surface as chemisorbed water molecules and the two others were physisorbed water molecules. Proton transfers are not included in the general reaction coordinates we designed. Nevertheless, the inspection of the trajectory shows that these early-stage steps of
the hydration are accompanied with the deprotonation of some of the coordinated water molecules and a widespread reshuffling of surface protons over about 1 nm (compare Fig. 2a, d). The amphoteric character of the hydrated material allows γ-Al₂O₃ to offer the proper local protonation level for the intermediates involved in its own decomposition into AlOₓHᵧ. In this respect, the trajectory reveals that physisorbed water molecules are involved, via a Grotthus mechanism, in this redistribution of surface protons. Physisorbed water molecules do therefore not only react but also help accommodating the protonation state of the surface to guest the final octahedral intermediate. This is particularly striking for the water fragments bound to the octahedral Al(1) and Al(2), which need to be deprotonated to coordinate the fleeing tetrahedral Alβ. This study highlights the key role of water as a reactant and as a solvent in the stability of an oxide and pre-figures the role of the pH in the interface transformation. Ab initio metadynamics can hence provide a complete atomistic picture of the alteration mechanism of an ionic-covalent solid in contact with a reactive solvent.

**Simulation with chemisorbed xylitol.** We have performed the same simulation substituting the water fragments bound to the octahedral Al(1) and Al(2).
Fig. 3 Inhibition of the decomposition of \( \gamma \)-Al\(_2\)O\(_3\) in the presence of chemisorbed xylitol. a \( \gamma \)-Al\(_2\)O\(_3\)(110)/water interface with the average occupation volume of water in gray. b Geometry of adsorbed xylitol at the \( \gamma \)-Al\(_2\)O\(_3\)(110)/water interface with the iso-surface of the average occupation volume of xylitol in ochre, and the average occupation volume of water in gray. The iso-surfaces were computed from an extra regular ab initio molecular dynamics simulation. More details can be found in Supplementary Note 8. c Free energy surface obtained from the metadynamics simulation on Al\(_{\beta}\) in presence of xylitol. CNa is the coordination number of Al\(_{\alpha}\) to alumina oxygen atoms. CNw is the coordination number of Al\(_{\beta}\) to water and polyols oxygens. Yellow and white balls represent aluminum and hydrogen atoms, respectively. The color red is used for alumina oxygen atoms and the associated CNw. The color blue is used for water oxygen atoms in gray.

Octahedral Al\(_{\alpha}^{(1)}\) and Al\(_{\alpha}^{(2)}\), which are in close vicinity to the water-sensitive tetrahedral Al\(_{\beta}\) with xylitol. The choice of the adsorption geometry (Fig. 3b and other views in Supplementary Fig. 7) is globally in agreement with earlier studies on polyol adsorption on alumina (Supplementary Note 8)\(^{29}\). The reactivity of Al\(_{\beta}\) is described using again the coordination number of Al\(_{\beta}\) to alumina oxygen atoms (CNa) as a variable. Since now, oxygen atoms are also found in xylitol, we considered, as a second variable, the coordination number to all other oxygen atoms that are external to alumina (oxygen atoms of water molecules and polyol) and referred to as CNw+p. The resulting free energy landscape in the presence of xylitol (Fig. 3c) is profoundly modified compared to the uncoated case (Fig. 2c). Despite the exploration of a 200 kJ mol\(^{-1}\) energy span, the sampled (CNa,CNw+p) space is reduced, meaning that Al\(_{\beta}\) is more constrained near its initial geometry at (CNa,CNw+p) = (3,1). A detailed look at the free energy landscape shows nevertheless that Al\(_{\beta}\) is able to react with some surrounding oxygen atoms (CNw+p goes up to 4). The exact mechanism is however very different from that described above. With xylitol adsorbed, CNa first decreases from 3 to 2 and CNw+p increases from 1 to 2, without any clear minimum in-between. This corresponds to a S\(_0\)-2 mechanism with a strong S\(_0\)-1 character where the Al\(_{\beta}\) leaches first from alumina to the outer surface (CNa decreases) before gaining an Al–O bond with water or xylitol (CNw+p increases). As discussed above, the hydration of Al\(_{\beta}\) follows an addition/elimination mechanism in the absence of xylitol. In other words, while a water molecule could easily reach the Al\(_{\beta}\) and perform a nucleophilic addition in absence of xylitol, it has become more difficult in presence of xylitol. The nucleophile must therefore either be immobilized or have difficulties to approach Al\(_{\beta}\). This is indeed confirmed by the inspection of the trajectories: Al\(_{\beta}\) does not react with physisorbed water molecules but rather with the chemisorbed alcohol moieties of xylitol. This frustrated extraction of Al\(_{\beta}\) out of the alumina surface is highly activated and shows a barrier of 161 kJ mol\(^{-1}\), consistent with the experimentally observed inhibiting power of xylitol for hydroxides formation.

To better understand why Al\(_{\beta}\) reacts with xylitol rather than water, we have performed a 25 ps long regular ab initio molecular dynamics simulation of the interface with xylitol adsorbed and compared to our recently published study work on the \( \gamma \)-Al\(_2\)O\(_3\)(110)/water interface\(^{33}\). The volume visited by physisorbed water molecules around Al\(_{\beta}\) is greatly impacted by the presence of xylitol as shown in Fig. 3a, b. This is further confirmed by the radial distribution functions of Al\(_{\beta}\) with physisorbed water molecules: the probabilities of finding physisorbed water molecules in the second coordination shell are indeed reduced and shifted to larger distances (Supplementary Fig. 8). This clearly evidences an important steric hindrance induced by xylitol, which is at the origin of the inhibition.

Once Al\(_{\beta}\) sees its coordination number to alumina oxygen atoms diminished by one unit, it directly coordinates to two alcohol groups because of the constrained adsorption mode of xylitol (CNw+p increases by two units). The resulting square-based pyramidal structure readily captures a water physisorbed molecule to gain a saturated octahedral geometry, reaching (CNa, CNw+p) = (2,4). Two other adsorption modes of xylitol, which substitute the chemisorbed water molecules involved in the decomposition mechanism, have been tested. They both turn out to be able to inhibit the early stages of the decomposition, proving that the inhibition shown here does not depend on the orientation of the tridentate adsorbate, in spite of mechanistic differences as discussed in Supplementary Note 9.

Noticeably, the inhibitor does not directly interact with the weak spot, but with a neighboring site, thereby modifying the interfacial structure of the liquid. It substitutes the water molecules that are
involved in the first hydration steps and prevents the necessary proton reshuffling to generate AlO$_2$H$^\cdot$ and therefore provides a strong stabilization of the surface of alumina. This is attributed to the γ-pentanetriol backbone of xylitol, a structural feature shared with sorbitol (a known good inhibitor) but not with glycerol (a known weak inhibitor). Our study therefore opens the road to a rational design of the structure of coating agents able to prevent γ-Al$_2$O$_3$ from decomposing in water.

In conclusion, the combined experimental and theoretical study presented here provides an atomistic mechanistic picture of the initial steps of the decomposition of γ-Al$_2$O$_3$ in water. The weak spot is a tetrahedral surface Al of the (110) surface. It undergoes successive addition of water/scission of Al-O, yielding to AlO$_2$H$^\cdot$. This process is accompanied by proton reshuffling. The chemisorption of a polyol on a neighbor site inhibits this hydrolysis by replacing the water molecules that initiate the process and by limiting the access of water to this weak spot. Noticeably, the weak spot of this oxide is not located at kink or edges but at the heart of a given facet. This understanding opens the road to further improvements or inhibitors. Since γ-Al$_2$O$_3$ is an iono-covalent oxide and water potentially reacts during the process and may dissociate into (OH$^-$. H$^+$), gaining such an atomistic understanding is a rather challenging task, especially regarding computational chemistry where the use of biased ab initio molecular dynamic is necessary. The present achievement thus constitutes an unprecedented milestone in the understanding of solid/liquid interface transformation. The approach that we propose here could be insightfully applied to various other relevant systems in electrochemistry, geochemistry or material science, where the reactivity of the solid with water and possibly other liquids plays a crucial role.

Methods

Alumina materials syntheses. Alumina C (for Commercial) was obtained by calcination of commercial boehmite (Sasol PURAL SB3) at 600 °C for 4 h. Alumina F (for Fibers) was synthesized by precipitation of aluminum nitrate (Al(NO$_3$)$_3$·9H$_2$O, 0.1 mol L$^{-1}$) in an aqueous medium. The pH was adjusted to an initial value of 8 by addition of sodium hydroxide (NaOH, 1 mol L$^{-1}$) and the resulting suspension was aged at 95 °C for 1 week. The final pH value of the suspension was 4.5. The solid was recovered by centrifugation and washed three times with water. This synthesis was adapted from the method described by Chiche et al. and Jolivet et al. Alumina P (for Plates) and R (for Rods) were obtained by an hydrothermal treatment of alumina C in water (alumina P) or in acidic medium, boehmite precipitates as rod-like nanoparticles. In neutral medium, boehmite precursors act as rod-like nanoparticles. In neutral medium, nanoparticles adopt a plate-like morphology. After cooling at room temperature (RT), the solid phase was recovered by centrifugation, dried at 100 °C overnight and calcinated at 600 °C for 4 h.

Material characterization. XRD analyses were performed on powders with a Bragg-Brentano diffractometer (Panalytical X’Pert PRO MPD) using Cu Ka radiation. Diffractionograms were obtained from 2θ = 4–74° with a step of 0.03° and 5 s per step. Textural properties of aluminas were determined by N$_2$ sorption studies at 77 K using a Micrometrics ASAP 2000 instrument. The BET method was applied to determine the specific surface area. Transmission electron microscopy (TEM) images were obtained on a JEOL 2010 LaB$_6$, microscope operating at 200 kV. A dispersion of the sample crushed in ethanol was deposited on standard holey carbon-covered TEM grids.

Adsorption experiments. Polyl adsorption isotherms were performed on three alumina materials exhibiting different morphologies in a 100 mL stainless steel autoclave equipped with a mechanical stirring rod (Top Industrie). Aqueous solutions of xylitol and sorbitol (0.5 g L$^{-1}$, 1 g L$^{-1}$, 2 g L$^{-1}$, 4 g L$^{-1}$, 6 g L$^{-1}$, and 8 g L$^{-1}$) were prepared using commercial polyls (Sigma Aldrich) and deionized water. Typically, 2 g of alumina were dispersed in 50 mL of an aqueous solution of polyol. After 2 h at 200 °C under autogenous pressure (14 bar) and vigorous stirring, a sample of the liquid phase was taken and the solid phase was recovered by centrifugation. The source data underlying Fig. 1d–f are available in SI. Raw data were generated at the PSMN and GENCi large-scale facilities. Derived data supporting the findings of this study are available as supplementary materials; a snapshot of two ab initio molecular dynamic runs is provided as well as the grid-based data of the Free Energy Surface that are plotted in Figs. 2c and 3c.

Received: 8 January 2019 Accepted: 17 May 2019
Published online: 17 July 2019

References

1. Sato, H., Miyagawa, Y., Okabe, T., Miyajima, M. & Sunada, H. Dissolution mechanism of diclofenac sodium from wax matrix granules. J. Pharm. Sci. 86, 929–934 (1997).
2. Maurice, V. & Marcus, P. Progress in corrosion science at atomic and environmental application: a review. Prog. Mater. Sci. 191, 132–171 (2018).
3. Chen, Z., Amine, R., Ma, Z.-F. & Amine, K. Interfacial reactions in lithium batteries. J. Phys. D. Appl. Phys. 50, 303001 (2017).
4. Fischer, C., Kurganskaya, I., Schafer, T. & Lüttge, A. Variability of crystal surface reactivity: what do we know? Appl. Geochemistry 43, 132–157 (2014).
5. Putnis, A. & Putnis, C. V. The mechanism of reorganisation of solids in the presence of a fluid phase. J. Solid State Chem. 180, 1783–1786 (2007).
6. Pirkannieminen, K. & Sillanpää, M. Heterogeneous water phase catalysis as an environmental application: a review. Chemosphere 48, 1047–1060 (2002).
7. Chheda, J. N., Huber, G. W. & Dumesic, J. A. Liquid-phase catalytic processing of biomass-derived alcohols as fuels and chemicals. Angew. Chem. Int. Ed. 46, 7164–7183 (2007).
8. Sievers, C. et al. Phenomena affecting catalytic reactions at solid–liquid interfaces. ACS Catal. 6, 8286–8307 (2016).
9. Skorina, T. & Allanore, A. Aqueous alteration of potassium-bearing aluminosilicate minerals: from mechanism to processing. Green. Chem. 17, 2123–2136 (2015).
10. Chen, G. et al. Successive interfacial reaction-directed synthesis of CeO2 @Au@CoO2–MnO2 environmental catalyst with sandwich hollow structure. ACS Appl. Mater. Interfaces 10, 11195–111603 (2018).

Data Availability

The source data underlying Fig. 1d–f are available in SI. Raw data were generated at the PSMN and GENCi large-scale facilities. Derived data supporting the findings of this study are available as supplementary materials; a snapshot of two ab initio molecular dynamic runs is provided as well as the grid-based data of the Free Energy Surface that are plotted in Figs. 2c and 3c.

Received: 8 January 2019 Accepted: 17 May 2019
Published online: 17 July 2019

References

1. Sato, H., Miyagawa, Y., Okabe, T., Miyajima, M. & Sunada, H. Dissolution mechanism of diclofenac sodium from wax matrix granules. J. Pharm. Sci. 86, 929–934 (1997).
2. Maurice, V. & Marcus, P. Progress in corrosion science at atomic and environmental application: a review. Prog. Mater. Sci. 191, 132–171 (2018).
3. Chen, Z., Amine, R., Ma, Z.-F. & Amine, K. Interfacial reactions in lithium batteries. J. Phys. D. Appl. Phys. 50, 303001 (2017).
4. Fischer, C., Kurganskaya, I., Schafer, T. & Lüttge, A. Variability of crystal surface reactivity: what do we know? Appl. Geochemistry 43, 132–157 (2014).
5. Putnis, A. & Putnis, C. V. The mechanism of reorganisation of solids in the presence of a fluid phase. J. Solid State Chem. 180, 1783–1786 (2007).
6. Pirkannieminen, K. & Sillanpää, M. Heterogeneous water phase catalysis as an environmental application: a review. Chemosphere 48, 1047–1060 (2002).
7. Chheda, J. N., Huber, G. W. & Dumesic, J. A. Liquid-phase catalytic processing of biomass-derived alcohols as fuels and chemicals. Angew. Chem. Int. Ed. 46, 7164–7183 (2007).
8. Sievers, C. et al. Phenomena affecting catalytic reactions at solid–liquid interfaces. ACS Catal. 6, 8286–8307 (2016).
9. Skorina, T. & Allanore, A. Aqueous alteration of potassium-bearing aluminosilicate minerals: from mechanism to processing. Green. Chem. 17, 2123–2136 (2015).
10. Chen, G. et al. Successive interfacial reaction-directed synthesis of CeO2 @Au@CoO2–MnO2 environmental catalyst with sandwich hollow structure. ACS Appl. Mater. Interfaces 10, 11195–111603 (2018).
