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Mechanistic investigations at the alumina/water interface

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PURPOSE OF THE ABSTRACT

gamma-Al₂O₃ has remarkable properties as a support, but it is very sensitive to water, either as a liquid[1] or even as steam[2]. This is preventing its usage when developing new heterogeneous catalysts to upgrade biomass. These structural changes can be retarded by the presence of polyols.[3] The mechanism of action of these additives is believed to lie in their chemisorption on the surface that would make gamma-Al₂O₃ water-resistant[3]. However, little is known on which exposed facet(s) and what site(s) need to be particularly targeted for protection. The optimization of the structure of inhibitors is therefore a challenging task since the exact mechanism of the decomposition of γ -Al₂O₃ in liquid water remains unknown. We combine here experiments and theory to provide the atomistic mechanism for the early-stage decomposition of gamma-Al₂O₃ in liquid water,[4] but also for the adsorption/desorption mechanism of (poly)-alcohols at the gamma-Al₂O₃ / water interface.[5]

Alumina samples containing particles with different shapes were exposed to a hydrothermal treatment in presence of various concentrations of polyol (sorbitol and xylitol, Fig 1b 1c). We experimentally determined the minimum surface coverage of polyol at which the decomposition of alumina gets inhibited, a quantity referred to as inhibiting coverage. Since this inhibiting coverage strongly correlates with the fractional area of the (110) facet of the alumina sample and only with this area, we concluded that the decomposition is initiated at the (110) facet (Fig 1d). Then, performing ab initio metadynamics simulations, we probed the reactivity of this Al₂O₃(110)/water interface and identified specific aluminum tetrahedral centers that are particularly reactive with water. We showed that interfacial water molecules are involved in the mechanism, both as reactants for the hydration of aluminum and as intermediates for the proton reshuffling required by the decomposition mechanism. We managed to determine the barriers (all lower than 80 kJ.mol⁻¹) for the 6 successive addition/elimination steps in a single simulation and the resulting final structure is shown in Fig 1e. Furthermore, the effect of xylitol was rationalized: its adsorption locally rendered the surface more hydrophobic and pushes water molecules away from the Al sites identified as water-sensitive.[4] Then, we investigated in details the adsorption/desorption mechanism of (poly)-alcohols at the gamma-Al₂O₃ / water interface and found that liquid water induces a barrier of at least 20kJ.mol⁻¹ due to the substitution of chemisorbed water and the solvent reorganization.[5]

Thanks to our advanced modeling, we located the weak spot of gamma-Al₂O₃ at the heart of the most exposed facet. It allowed us to improve the design of protective additives. Beyond its impact on the stability of this important support, the present achievement constitutes an unprecedented milestone in the understanding of solid/liquid interface transformation in term of methodology.

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FIGURES

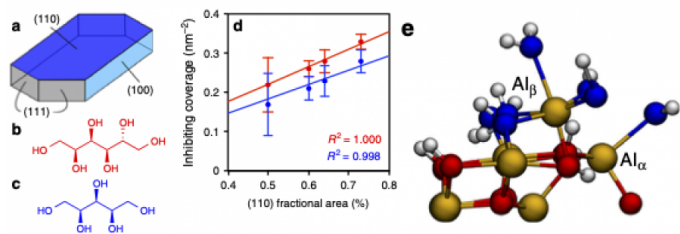


FIGURE 1

Protecting alumina with polyols from water weathering

FIGURE 2

KEYWORDS

Modelling | catalyst stability | alumina | water

BIBLIOGRAPHY