



Experiment title: Unravelling the chemistry of water adsorption on alumina by X-ray diffraction at glancing incidence	Experiment number: SI-540
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Shifts: 18	Local contact(s): DR Odile ROBACH (e-mail: robach@esrf.fr)	<i>Received at ESRF:</i> 21 MAR. 2000
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Names and affiliations of applicants (* indicates experimentalists):

Dr. Jacques JUPILLE Laboratoire mixte CNRS-St Gobain Recherche,
39, Quai Lucien Lefranc
93304 Aubervilliers,
France

Dr. Antoine BARBIER CEA-Grenoble, DRFMC/SP2M/IRS
17 rue des Martyrs, 38054 Grenoble Cédex 9

Dr. Martine GAUTIER-SOYER CEA/Saclay, DRECAM/SRSIM, 91191 Gif sur Yvette
Cedex, France

Dr. Gilles RENAUD CEA-Grenoble, DRFMC/SP2M/IRS
17 rue des Martyrs, 38054 Grenoble Cédex 9

Report:

The existence of chemisorbed hydroxyl groups at the surface of oxide substrates is of broad practical relevance. It plays a key role in catalysis, in adhesion, in corrosion, in the ageing of glass, ceramics and concrete but also in the chemistry of the soils and in the growth of plants. Clearly, many observations agree about the fact that water molecules do dissociate on oxide surfaces to give rise to hydroxylated surfaces. Surprisingly, it is only recently that surface analysis have been able to directly observe water dissociation on such substrates, namely TiO_2 , MgO and $\alpha\text{-Al}_2\text{O}_3$ surfaces. In the latter cases, the myopia of surface science came from the particular conditions which are required to produce stable hydroxylated layers, i.e. either high pressure (10^{-1} Pa on $\text{MgO}(100)$ [1,2] and 10^2 Pa on $\alpha\text{-Al}_2\text{O}_3$ (0001) [3]) with respect to the usual standard ($< 10^{-3}$ Pa) or, alternatively, adsorption of an ice layer below 150 K under low pressure conditions and further desorption of that layer at room temperature [2].

Model adsorbate-covered crystal substrates are at the origin of the development of surface studies about the reactivity of metal and semiconductor surfaces. The purpose of the present work is to define for the first time one such surface in the very important series of the hydroxylated ionocovalent substrates.

To date, most hydroxylation mechanisms are at the centre of running controversies involving measurements and theories. Water on $\alpha\text{-Al}_2\text{O}_3$ (0001) appears to be the only case in which experiment shows [2-4] and calculation predicts [5] dissociative adsorption. However, strong uncertainties on the reactivity of ionocovalent surfaces come from the existence of defects whose nature and concentration often escape analysis, so that the amount

of surface species adsorbed on these defects can not be estimated. Therefore, it should not only be proved that the reaction occurs, as it has been already done [2-4], but also that the reaction takes place on the ordered part of the α -Al₂O₃ (0001) surface.

An elegant manner to demonstrate that the "perfect" surface does react is to point to a structural change. Again, the α -Al₂O₃(0001) surface offers a nice opportunity to produce such an evidence. This surface is aluminium-terminated with a single aluminium plane [6,7]. X-ray diffraction at glancing incidence showed that the first four surface planes are strongly relaxed with respect to the bulk distances (- 51 % , + 16 % , - 29 % and + 20% [6]), in agreement with theoretical calculations [7].

It is predicted that hydroxylation should produce a large outward displacement of 0.061 nm for the aluminium surface atoms bonded to hydroxyl groups, while a much smaller relaxation of 0.026 nm is expected upon molecular adsorption of water [5].

Such large variation of the relaxation upon hydroxylation should be readily visible when comparing Crystal truncation rods of the clean surface and the hydroxylated surface.

The original CTR measurements [6,7] were thus reproduced using the high pressure chamber of the ID03 beamline. On the clean surface, the CTRs are basically identical to those already published.

Next, the measurements were redone three times with the following conditions:
-after having exposed the surface at to 10 Torr of water vapour, and re-pumped the system;
-under the 10 Torr of H₂O, without repumping nor interrupting the beam;
-under the 10 Torr of H₂O and exposure to the x-ray beam only during counting.

In all three case, the measured CTRs were exactly identical to those of the non-hydroxylated surface.

We are presently reproducing the XPS measurements that proved that hydroxylation happened during water exposure at 10 Torr, **on the very same sample**, in order to try to understand whether hydroxylation effectively happened on the flat terraces during the measurements, but did not de-relaxed the surface, or whether hydroxylation only happens on defects, in which cases, it would not be visible through X-ray scattering measurements.

References

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