Supplementary Material (ESI) for Chemical Communications

Dinitrogen: a molecule to selectively probe Al_{III} defect sites on alumina

Raphael Wischert,[a,b] Christophe Copéret,*[a,b] Françoise Delbecq[b] and Philippe Sautet*[b]

[a)] Université de Lyon, Institut de Chimie de Lyon, C2P2, CNRS, CPE Lyon
43, Bd. du 11 Novembre 1918, F-69616 Villeurbanne Cedex (France).
Present address:
ETH Zürich, Department of Chemistry, Wolfgang Pauli Strasse 10,
CH-8093 Zürich (Switzerland), Fax: (+41) 446331325;
E-mail: ccoperet@inorg.chem.ethz.ch

[b)] Université de Lyon, Institut de Chimie de Lyon, CNRS, École Normale Supérieure de Lyon, 46 allée d'Italie, F-69364 Lyon Cedex 07 (France), Fax: (+33) 472728860;
E-mail: Philippe.Sautet@ens-lyon.fr

Experimental procedures

Aeroxide C alumina (XRD shows a mixture of δ- and θ phases, see Fig. S2) was purchased from Degussa. γ-Alumina (SBa-200) was donated by SASOL Germany GmbH. Nitrogen (Alphagaz 1) was purified over Cu (BASF R3-11 catalyst) and MS 4 Å in order to remove O_2 and H_2O. All experiments were carried out on a high vacuum line (1.77×10^{-3} Pa), equipped with a mercury diffusion pump. For glass connections high vacuum Apiezon H grease was used. IR spectra were recorded on a Nicolet spectrometer and treated with the OMNIC software.

Adsorption of N_2 on alumina was monitored by transmission IR spectroscopy. We use a quartz glass reactor for the thermal treatments, on which a head with CaF_2 windows can be mounted. A pellet (ca. 50 mg) was prepared from alumina and calcined in air in a tubular furnace at 500 °C (heating rate 4 °C / min) for 18 h. The cell head was then mounted on the glass reactor keeping the reactor at 500 °C. The sample was subsequently evacuated at a given temperature for 12 h (heating rate 4 °C/min) and allowed to cool down to room temperature prior to acquisition of an IR spectrum of Al_2O_3. Then, N_2 (56 hPa) was added and a spectrum was recorded 5 min later.

Theoretical methods

The DFT calculations were performed in periodic boundary conditions in the Generalized Gradient Approximation (GGA) using the Perdew-Wang (PW91) functional[1], as implemented in the VASP code (version 4.6)[2]. The Projected Augmented Wave (PAW)[3] method was adopted for the description of atomic cores. For N a small radius for the core (1.1 a.u.), associated with a high cut-off energy of 700 eV, was necessary in order to accurately reproduce the structural and vibrational properties of the N_2 molecule. We use a γ-Al_2O_3 model described earlier by some of us [4]. An 8-layers thick slab (unit formula $Al_{16}O_{32}$) was used, with an inter-slab distance of *ca.* 20 Å. The Brillouin zone integration is performed with a 3 × 3 × 1 k-point grid generated by the Monkhorst-Pack algorithm[5]. In order to reproduce the properties of extended surfaces, the bottom two layers were kept fixed during the calculations at bulk coordinates, while the top layers were allowed to relax. The frequencies are predicted using a harmonic approach. The Hessian matrix is calculated by a numerical finite-difference method, displacing each ion by +/−0.02 Å from its equilibrium position in the three directions of space. For these calculations only the first layer of alumina was considered. AIM calculations were carried with out a program available on the Internet (http://theory.cm.utexas.edu/vtsttools/bader/)[6].

[1] J. P. Perdew, Y. Wang, *Phys. Rev. B* **1992**, *45*, 13244.
[2] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169.; G. Kresse, J. Hafner, *Phys. Rev. B* **1993**, *47*, 558.
[3] P. E. Blöchl, *Phys. Rev. B* **1994**, *50*, 17953.
[4] M. Digne, P. Sautet, P. Raybaud, P. Euzen, H. Toulhoat, *J. Catal.* **2004**, *226*, 54.
[5] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **1976**, *13*, 5188.
[6] W. Tang, E. Sanville, and G. Henkelman, *J. Phys.: Condens. Matter* **2009**, 21, 084204.

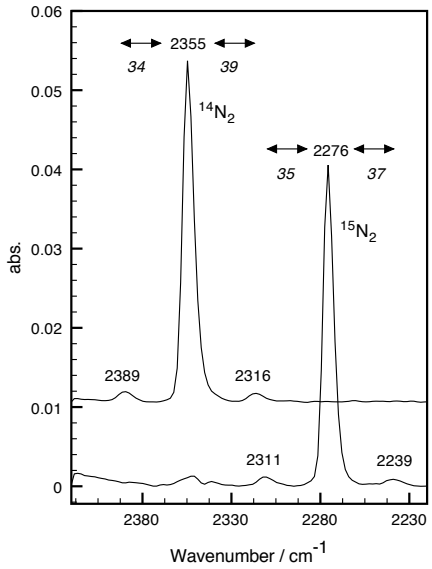


Figure S1 IR spectra of Degussa C alumina pretreated at 500°C under vacuum (1.77×10^{-3} Pa) after contact with $^{14}N_2$ or $^{15}N_2$ (65 kPa).

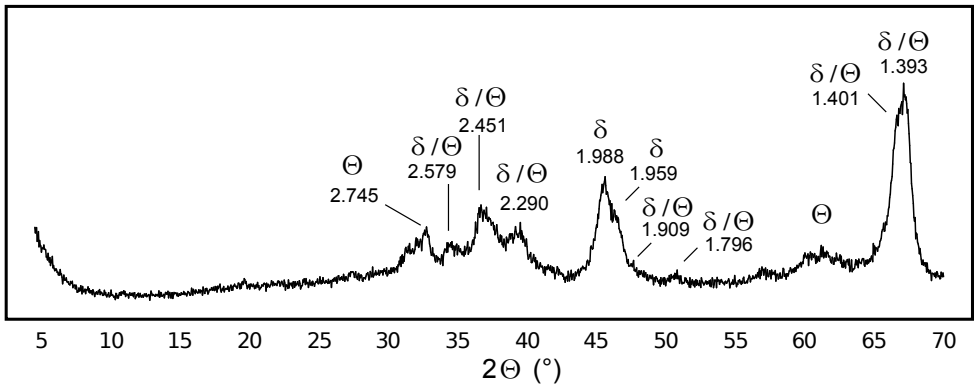
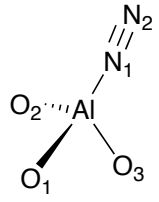


Figure S2 Powder X-Ray diffractogram of Degussa C alumina after treatment at 500 °C.

Table S1 Results of the Bader charge analysis.



System	Al_{III}	N_1	N_2	O_1	O_2	O_3
N_2/Al_{III} (**s0**)	+2.423	–0.166	+0.151	–1.584	–1.584	–1.648
s0	+2.396			–1.587	–1.586	–1.651
s0 (relaxed)	+2.403			–1.589	–1.587	–1.657