LETTER

Catalyst support effects on hydrogen spillover

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Hydrogen spillover¹ is the surface migration of activated hydrogen atoms from a metal catalyst particle, on which they are generated, onto the catalyst support². The phenomenon has been much studied³⁻⁷ and its occurrence on reducible supports such as titanium oxide is established, yet questions remain about whether hydrogen spillover can take place on nonreducible supports such as aluminium oxide⁸⁻¹³. Here we use the enhanced precision of top-down nanofabrication^{14,15} to prepare controlled and precisely tunable model systems that allow us to quantify the efficiency and spatial extent of hydrogen spillover on both reducible and nonreducible supports. We place multiple pairs of iron oxide and platinum nanoparticles on titanium oxide and aluminium oxide supports, varying the distance between the pairs from zero to 45 nanometres with a precision of one nanometre. We then observe the extent of the reduction of the iron oxide particles by hydrogen atoms generated on the platinum using single-particle in situ X-ray absorption spectromicroscopy¹⁴ applied simultaneously to all particle pairs. The data, in conjunction with density functional theory calculations^{16,17}, reveal fast hydrogen spillover on titanium oxide that reduces remote iron oxide nanoparticles via coupled proton-electron transfer. In contrast, spillover on aluminium oxide is mediated by three-coordinated aluminium centres that also interact with water and that give rise to hydrogen mobility competing with hydrogen desorption; this results in hydrogen spillover about ten orders of magnitude slower than on titanium oxide and restricted to very short distances from the platinum particle. We anticipate that these observations will improve our understanding of hydrogen storage^{18,19} and catalytic reactions involving hydrogen^{8,11-13}, and that our approach to creating and probing model catalyst systems will provide opportunities for studying the origin of synergistic effects in supported catalysts that combine multiple functionalities.

The different approaches to studying hydrogen spillover^{5–7,20–22} are often limited in their visualization of the phenomenon, primarily owing to a lack of well defined model systems with clearly separated catalytic functions. For example, an often used system comprises metal particles added to a nonreducible oxide support and then physically mixed with a reducible oxide^{3,8,9}, which means that movement of particles from one oxide to another and direct contact of the metal with the reducible support cannot be excluded and that the distance between the catalytic particles remains undefined. And although a reducible metal oxide in direct contact with a metal catalyst has been shown to reduce during hydrogen dosage²³, it is unknown whether a remote metal oxide not in direct contact with the metal can also be reduced by spillover⁸.

Figure 1 illustrates our approach to studying hydrogen spillover, which makes use of state-of-the-art electron beam lithography (EBL)¹⁴ to produce well defined nanoparticles that are then monitored *in situ* using spatially resolved X-ray absorption spectroscopy (XAS) in a X-ray photoemission electron microscope (X-PEEM)^{14,24,25}. This allows us directly to observe chemical transformations induced by hydrogen spillover (sketched in Fig. 1a) in well defined model systems, comprised

of different supports onto which we place pairs of iron oxide and platinum nanoparticles at varying distances from each other (Fig. 1b). Figure 1c shows the scanning electron microscope (SEM) image of the nanofabricated model on an aluminium oxide support (2 nm thick alumina) which is an exact one-to-one representation of the design in Extended Data Fig. 1a.

The 16 distinct model systems, in a $3 \times 3 \mu m^2$ field of view, consist of a total of 15 platinum–iron oxide nanoparticle pairs in which the distance between the two particles increases from 0 nm for the overlapping pair 'a1' to 45 nm for the farthest-separated pair, with the distance incrementing by 5 nm or 10 nm; and a lone iron oxide nanoparticle without platinum in its vicinity (system 'd4'). Starting from pair 'a1', where the centre of the iron oxide particle coincides with the centre of the platinum particle, the distance between the two particles increases: pair 'b1' shows partial overlap, the two particles almost meet in pair 'c2', and the maximum separation distance of 45 nm is reached in pair 'd3'. Higher-magnification SEM images of two of the particle pairs,



Figure 1 | Fabrication and single-particle spectromicroscopy of the model system to observe hydrogen spillover. a, Scheme of hydrogen spillover from platinum to an iron oxide particle over a titanium oxide or aluminium oxide support. b, Model consisting of pairs of platinum and iron oxide particles with varying interparticle distances *d* and a lone iron oxide particle on a single support. c, SEM image of the nanofabricated model system on an aluminium oxide support, with 15 such pairs and a single iron oxide particle over an area of $3 \times 3 \mu m^2$ (scale bar, 500 nm). The iron oxide particles have a diameter of 60 nm, while the platinum particles have a diameter of 30 nm. The distance between the pairs is 1 μ m. d, e, Higher-magnification SEM images (scale bars, 25 nm) of pairs 'd1' and 'a1', encircled in green and red, respectively. f, X-PEEM image of the sample recorded at the Fe L₃ edge, which shows each of the 16 systems probed simultaneously by single-nanoparticle XAS (scale bar, 500 nm).

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encircled in Fig. 1c, are shown in Fig. 1d and e: the pair 'd1' with a distance of 25 nm between the platinum nanoparticle and the iron oxide nanoparticle, and the overlapping pair 'a1'. Our approach to fabricating the nanoparticle pairs, with a particle thickness of 2 nm, circumvents the limitations of EBL²⁶ (Extended Data Fig. 1c) so that we can tune the distance between the platinum nanoparticle of diameter 30 nm and the iron oxide nanoparticle of diameter 60 nm with a precision of 1 nm. This approach was also used to produce an equivalent model system using a 5-nm-thick anatase titanium oxide (titania) support (Extended Data Fig. 1b).

To observe any hydrogen spillover during hydrogen dosage, a surface-sensitive and space-resolved in situ single nanoparticle iron L₃ edge XAS measurement is performed simultaneously on each of the 16 iron oxide particles to reveal their degree of reduction as a function of distance from the platinum particle. Figure 1f is the X-PEEM elemental contrast image at the iron L₃ edge acquired at the base pressure and provides a spatial map of the X-ray absorption cross-section and, thus, the chemical fingerprint of the sample (see Supplementary Video). Since platinum and the support have no absorption edge at this energy, only the iron oxide particles are visible. Depending on whether or not spillover onto the support takes place, the iron oxide particles at different distances from the platinum may or may not undergo reduction, thus interconverting iron oxides and giving rise to the evolution of metallic iron. The extent of reduction is visible in the XAS spectra as increased intensity at the iron L₃ absorption edge, corresponding to a relative decrease in the resonant oxide peak, which is further quantified by linear combination fitting¹⁴.

The iron L₃ edge XAS spectra at room temperature of all iron oxide particles coincide (Extended Data Fig. 2), consisting mainly of iron(II,III) oxide and no metallic iron; during hydrogen dosage, the amount of reduction of the iron oxide in the different pairs on the nonreducible aluminium oxide support varies. Figure 2a shows the spectra from three selected pairs and the lone iron oxide particle at 343 K. As expected, the iron oxide particle overlapping with the platinum particle (pair 'a1') is reduced significantly because the hydrogen atoms do not have to spillover via the support and linear combination fitting reveals that this yields 16.8% of metallic iron phase (Extended Data Fig. 3). The lone iron oxide particle (system 'd4') has a much lower intensity at the iron L_3 absorption edge ('P1' in Fig. 2a) and does not undergo reduction to metallic iron, which indicates it has not been reached by spillover hydrogen. Likewise, the XAS spectra of iron oxide nanoparticles in pairs 'd3', 'd2' and 'd1' with interparticle distances of 45 nm, 35 nm and 25 nm, respectively, coincide with the XAS of the lone iron oxide particle of system 'd4', providing a direct proof that no spillover of hydrogen atoms occurs on aluminium oxide over such distances. However, as the distance between the two nanoparticles approaches 15 nm in pair 'c4', there is a slight reduction of iron oxide (Fig. 2a). The reduction in this pair is less than in the overlapping pair 'a1', which has higher intensity at the iron L₃ absorption edge; for these two cases, the extent of reduction of iron oxide increases as the distance between the particles decreases. Pair 'a1' yields a degree of conversion to metallic iron 14 times higher than in pair 'c4', which has 1.2% of metallic iron; there is no conversion in pairs beyond this distance (Extended Data Fig. 3).

Taken together, the data provide compelling proof of a reduction gradient on aluminium oxide support: reduction due to spillover occurs over very short distances from the metal catalysts but not at distances greater than 15 nm (Fig. 2b). In terms of hydrogen concentration, the most-reduced iron oxide particle in pair 'a1' comes into contact with all the dissociated hydrogen atoms produced on the platinum particle. For interparticle distances of 5 nm and 15 nm, in which pairs the iron oxide particle is reduced by 2.8% and 1.2%, respectively, this corresponds to 16.7% and 7.1% of the hydrogen atoms used in the case of maximal reduction as achieved in pair 'a1'; at greater distances, contact with hydrogen atoms is inconsequential. Because the extent of reduction depends on the concentration of hydrogen atoms on the aluminium



Figure 2 | **Hydrogen spillover on the aluminium oxide support. a**, XAS spectra at the Fe L₃ edge measured in X-PEEM during hydrogen dosage at 1×10^{-5} mbar, demonstrating the degree of reduction of the iron oxide particles on the aluminium oxide support for three selected pairs (an overlapping pair of iron oxide and platinum particles, and the pairs with interparticle distances of 15 nm and 45 nm) and the iron oxide particle without platinum in its vicinity. The legend of the graph corresponds to the colour of the circles around the systems in the SEM image (inset). b, Platinum–iron oxide pairs at varying distances *d* and a lone iron oxide particle on a single support, demonstrating the distance-dependent hydrogen spillover on the aluminium oxide support from the initial state in Fig. 1b. The percentage of the total composition of each particle at 343 K that is in the metallic iron phase, which forms owing to the reduction of the iron oxides from the platinum particle.

oxide surface that is available to each iron oxide particle, we probe the aluminium oxide support using Al K edge XAS (Extended Data Fig. 4a) and find evidence for characteristic three-coordinated surface aluminium adsorption sites (Al3c)²⁷, which are known to be responsible for hydrogen adsorption²⁸ and are likely to mediate the spillover effect.

On the reducible titanium oxide support, *in situ* iron L_3 edge XAS spectra are taken at regular intervals during hydrogen dosage of all 16 systems and the structural change in the support around each pair is also probed with spatial resolution at the Ti $L_{2,3}$ edge. Figure 3a compares the two extreme cases: Fe XAS spectra of the overlapping pair 'a1' and of the pair 'd3' with its particles separated by 45 nm. The XAS spectra of both pairs coincide at the initial state (state 1), and also after dosing hydrogen at 343 K (state 2, when iron oxide in both pairs is reduced equally). Irrespective of the distance from the platinum particle, all iron oxide particles on the support are uniformly reduced (including the particle with no neighbouring platinum particle within a distance of 1 µm; Extended Data Fig. 5).

Linear combination fitting reveals the evolution of 17% metallic iron at this stage (Extended Data Fig. 6). Furthermore, the titanium oxide XAS spectra²⁹ show uniform reduction from Ti^{4+} to Ti^{3+} over its



Figure 3 | Hydrogen spillover on the titanium oxide support. a, Fe L₃ XAS spectra compares the extent of the reduction of iron oxide on a titanium oxide support in the pair 'd3' with an interparticle distance of 45 nm and the overlapping pair 'a1', circled in green and red, respectively, in the SEM image (inset). After hvdrogen dosage at 1×10^{-5} mbar pressure in X-PEEM at 343 K, the initial state XAS (state 1) and the reduced state XAS (state 2) of both pairs overlap. **b**, The Ti $L_{2,3}$ edge XAS of the initial state and after hydrogen spillover from platinum at 343 K. Equal surface reduction takes place around all 16 systems and in an isolated area far from the platinum (inset, SEM image). c, The Ti L_{2.3} edge XAS spectra of the initial state and after hydrogen dosage up to 425 K for a sample without platinum nanoparticles. There is no observable reduction of titanium oxide. d, Illustration of spillover on titanium oxide at 343 K from the initial state in Fig. 1b. All the iron oxide particles as well as the titanium oxide support reduce simultaneously, irrespective of their distance d from the platinum particles. A maximum reduction of 17% occurs for all iron oxide particles at this stage.

surface (Fig. 3b) for all 16 systems and even at a large distance from the platinum catalyst (Extended Data Fig. 7). A control experiment using a fresh sample of titanium oxide lacking platinum particles resulted in no support reduction with hydrogen dosage at temperatures up to 425 K (Fig. 3c), confirming the crucial role of both the platinum particles and the fast spillover of the dissociated hydrogen atoms onto and subsequent diffusion over the support until equilibrium is reached. The hydrogen atoms then react with each of the iron oxide particles, regardless of their distance from the platinum nanoparticles (Fig. 3d).

To probe the mechanism of hydrogen adsorption and migration on anatase titanium oxide and the γ -aluminium oxide supports, we use first-principles atomistic simulations^{16,17} that show spontaneous dissociation of hydrogen on the platinum cluster independent of the support (Fig. 4a). Under the experimental conditions (Extended Data Fig. 8), the barrier for spillover of dissociated hydrogen onto anatase is 0.45 eV. A slightly higher proportion of energy, between 0.6 eV and 0.7 eV, is required to transfer an electron and a proton among the different titanium oxide sites (Fig. 4b), which yields a diffusion coefficient D of $4.2\times10^{-14}\,{\rm cm}^2\,{\rm s}^{-1}$ at 300 K. This mobility is not influenced by the presence of water on the surface (Fig. 4b, Extended Data Figs 8 and 9) and desorption of hydrogen, requiring about 2.45 eV (Extended Data Fig. 10), is energetically improbable. The combination of these factors results in an almost instantaneous reduction of the titanium oxide across the surface, leading to the reduction of iron oxide particles, independent of their distance from platinum (Fig. 3).

On aluminium oxide³⁰, both water and hydrogen adsorb dissociatively with formation of OH^- and H^- species, respectively. These species compete for the same Al3c adsorption sites as those exposed on the [100] interface and that are fundamental for aluminium oxide reactivity (Methods and Extended Data Figs 4 and 10). The more water there is, the lower is the amount of Al3c sites and the lower is the hydrogen coverage²⁸. Spectroscopic evidence of such sites (Extended Data Fig. 4a), with well established²⁸ water-dependent availability (Extended Data Fig. 4b), supports the idea that not all undercoordinated aluminium sites are hydrated under the experimental conditions. The transfer of the reducing species between neighbouring aluminium oxide sites has an activation energy barrier ranging from 1.15 eV to 1.63 eV, depending on the hydration of the surface (Fig. 4c). Furthermore, the hydrogen desorption energy of dehydrated aluminium oxide is 1.55 eV and can be as low as 0.38 eV for aluminium oxide with high water coverage (Extended Data Fig. 10). The hydrogen desorption rate is, therefore, faster or comparable to the surface mobility, causing a gradient in hydrogen coverage of the surface.

Thus, in agreement with previous theoretical and experimental work^{28,30}, our calculations (Extended Data Fig. 4b) suggest that there is a strong effect of water on aluminium oxide and that hydrogen mobility on its surface is much more restricted than on titanium oxide, with a diffusion coefficient of 1.4×10^{-23} cm² s⁻¹ at 300 K (which is about 10^{10} times lower than the corresponding diffusion coefficient on titanium oxide). The lower activation energy for detachment of hydrogen in competition with the slow hydrogen diffusion leads to a rapidly decreasing hydrogen concentration as the distance from platinum increases and in accordance with the distance-dependent reduction of the iron nanoparticles (Fig. 2).

In summary, our work clearly documents the efficiency of hydrogen spillover on reducible surfaces such as titanium oxide: it gives rise to uniform support reduction and even reduces a remote metal oxide that is not in direct contact with the platinum catalyst, irrespective of distance. Spillover on the nonreducible support aluminium oxide is vastly slower and limited to short distances, with the hydrogen flux decreasing over distance to create a concentration gradient. Looking forward, we anticipate that the use of nanofabrication of a unique model system in combination with single-particle spectroscopy will also prove valuable when exploring other fundamental questions in heterogeneous catalysis.





Figure 4 | The most relevant mechanisms of hydrogen adsorption and migration on titanium oxide (101) and γ -aluminium oxide (100). The method used was nudged elastic band (NEB); see Methods. The results corroborate experimental observations. All energies are normalized to the energy of the isolated hydrogen molecule in the gas phase. In the ball-andstick models the main stages of hydrogen adsorption and migration are illustrated. A is the gas-phase hydrogen molecule. C is hydrogen adsorbed on the metal oxide. D and E are intermediate configurations. Labels with an asterisk refer to transition states. Labels C-C' and D-D' denote equivalent sites. The labels A-E in the energy diagrams correspond to the configurations shown in the models above. Colour-coding in the ball-andstick models: red, O; yellow, H; silver, Ti; blue, Pt; and cyan, Al. Filled Ti 3d orbitals are indicated by a blue density surface. a, Hydrogen dissociation (activation energy E_{act}) on the platinum cluster and spillover to anatase titanium oxide (steps A–D–E–C of above model): $0.9 > E_{act} > 0.0 \text{ eV}$, depending on the hydrogen coverage of the cluster (red, 1H:1Pt; yellow, 2H:1Pt; and green, 3H:1Pt). b, Combined electron-proton mobility on the anatase slab (steps C–C' of above model): $E_{act} = 0.7$ eV, in the absence (black) and presence (blue) of water. c, Hydride mobility on γ -aluminium oxide (steps C–D–D'–C' of above model): maximum $E_{act} = 1.63 \text{ eV}$ (clean surface, red) and $E_{act} = 1.15 \text{ eV}$ (hydrated surface, blue).

Online Content Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to these sections appear only in the online paper.

Received 20 May; accepted 3 November 2016.

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Supplementary Information is available in the online version of the paper.

Acknowledgements Part of this work was performed at the Swiss Light Source, Paul Scherrer Institute, Switzerland. We acknowledge the Swiss Light Source for providing synchrotron radiation beamtime at the Surfaces/ Interfaces Microscopy beamline. We thank S. A. Tschupp for his assistance during beamtime, V. Guzenko for technical support with the EBL tool, M. Wipf for atomic layer deposition, and M. Ranocchiari and M. Schoenberg for their comments on the manuscript. The Paul Scherrer Institute (PSI) Research Commission provided financial support through the CROSS programme. J.A.v.B. thanks the NCCR MUST and J.V. acknowledges financial support by the European Union FP7 in the form of an ERC Starting Grant (contract number 277910). Calculations were supported by a grant from the Swiss National Supercomputer Center (Project ID ch5).

Author Contributions J.A.v.B., J.G. and Y.E. conceived the project. W.K. wrote beamtime proposals and planned the study with J.A.v.B. and Y.E. W.K. developed the model systems under the guidance of Y.E. and J.A.v.B. W.K. carried out the experiments at the beamline with technical support from A.K. Analysis and interpretation of the data were done by W.K. and J.A.v.B. C.S. conducted the density functional theory (DFT) simulations under the guidance of J.V. W.K. wrote the manuscript with contributions from all authors.

Author Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to J.A.v.B. (jeroen.vanbokhoven@chem.ethz.ch) or Y.E. (yasin.ekinci@psi.ch).

Reviewer Information *Nature* thanks E. van Steen and the other anonymous reviewer(s) for their contribution to the peer review of this work.

METHODS

Top-down nanofabrication of model systems. Although a number of studies have tackled spillover using approaches such as single-particle surface plasmon spectroscopy⁷, resonant photoemission spectroscopy²⁰, infrared spectroscopy²², scanning tunnelling microscope imaging²¹ and the 'molecular cork' effect⁵, others have introduced designs of model systems using platinum-encapsulated alumino-silicates⁶. Model systems that adhere to the accepted definition of hydrogen spillover should, ideally, incorporate a metal catalyst and the reacting species on the same support with precise positioning of particles without contamination (Fig. 1a), and this has to be probed in order to observe the spillover of hydrogen between them.

We employed top-down nanofabrication to create model systems containing pairs of particles at precisely defined distances on aluminium oxide (alumina) and titanium oxide (titania), a nonreducible and a reducible support respectively. Fabrication of the model system was based on the design in Extended Data Fig. 1a. The exact one-to-one match between the design and the model system was achieved on aluminium oxide and titanium oxide supports (SEM images in Fig. 1c and Extended Data Fig. 1b) by means of a three-step EBL overlay exposure shown in the scheme in Extended Data Fig. 1c. The supports were prepared by atomic layer deposition at 500 K of the 5-nm-thick layer of titanium oxide and the 2-nm-thick layer of aluminium oxide on a 1×1 cm² silicon wafer with its native oxide. A thin film of aluminium oxide was obtained using trimethylaluminum precursor³¹ in the Ultratech/Cambridge NanoTech atomic layer deposition system. The tetrakis (dimethylamido)titanium(IV) precursor yields anatase titanium oxide³². These thin films helped to overcome the charging associated with insulating substrates, such as oxides and semiconductors, during measurements in the X-PEEM. Once the support was prepared, the first EBL step at the Vistec EBPG 5000PlusES tool involved fabrication of markers on the support, which helped with alignment of the tool for further lithography steps and processing. Further processing steps are shown in Extended Data Fig. 1c, which initially involved spin-coating of poly (methyl methacrylate) (PMMA) resist (Extended Data Fig. 1c (i)). This was followed by EBL exposure of nanoholes using proximity effect correction (Extended Data Fig. 1c (ii)), thermal deposition of iron (Extended Data Fig. 1c (iii)), and lift-off resulting in a 4×4 array of iron nanoparticles with diameter 60 nm and thickness 2 nm (Extended Data Fig. 1c (iv)).

Exposure of iron(0) to the ambient environment after sample preparation leads to the oxidation of the particles to iron oxide. The exposure to ambient air does not occur instantaneously. Instead, our samples are situated in a vacuum chamber, which after successful sample preparation, is gradually vented to atmospheric pressure over half an hour. The resulting chemical reaction heat is therefore only gradually released and there is sufficient time for the nanostructures to equilibrate thermally with the substrate, which is held at room temperature. Using the alignment markers, a third EBL step was performed on PMMA in a similar manner (Extended Data Fig. 1c (v)) with nanoholes positioned at varying distances from the iron oxide nanoparticles (Extended Data Fig. 1c (vi)), followed by electron-beam-assisted physical vapour deposition of platinum (Extended Data Fig. 1c (vii)) and lift-off to achieve platinum nanoparticles of diameter 30 nm and thickness 2 nm (Extended Data Fig. 1c (viii)). This resulted in the desired pairs of iron oxide and platinum nanoparticles.

Sub-10-nm resolution is difficult to achieve using EBL²⁶ and, despite the usage of alignment markers, multiple EBL steps can result in a positioning error of \pm 30 nm in both axes, depending on the regulated design of the alignment markers and the charging effects associated with the substrate, which is well below the required precision for the interparticle distance. To circumvent this problem, we applied an approach that involved fabrication of a large array of the model system (Extended Data Fig. 1a) on the same support. This was done using a 13 × 13 array of the model in Extended Data Fig. 1a, each separated by $10\,\mu$ m. The centre of the array corresponds to the design in Extended Data Fig. 1a and the platinum particles are shifted by 2 nm on the right, left, bottom and centre in the models in the respective directions, whereas the 16 iron oxide particles do not change position. Therefore, the drift of the electron beam in overlay exposure is compensated in the x-y direction by scanning all errors greater than 1 nm. Since the random EBL error is constant during an overlay exposure step, we scan all possible errors. In this way, one of the 169 models on the surface always corresponded to exactly the design in Extended Data Fig. 1a, determined by SEM analysis after nanofabrication and the distance is also measured with 1 nm precision. This gave complete control over interparticle distance and the correct sets of dimers were identified for spectromicroscopy. This nanofabrication strategy yields a precision of 1 nm for particle placement, which resulted in the same model system on both the supports, demonstrating very high reproducibility. Such model surfaces with two particles separated by a controlled distance on a single support present a unique opportunity to elucidate chemical action at a distance from the metal in fundamental catalytic reactions.

X-PEEM and data analysis. The spectromicroscopy data was acquired in the X-PEEM at the Surfaces/Interfaces Microscopy beamline in the Swiss Light Source, which enabled single-nanoparticle XAS. To avoid interactions between the pairs and overlapping of their signals, the distance between the 16 iron oxide particles was $1\,\mu m$, since the X-ray PEEM has a spatial resolution 14,25,33 of about 50-100 nm. The particle thickness is chosen as 2 nm so that the whole particle is probed (the PEEM is a surface-sensitive technique probing a depth of about 3 nm). A field-of-view of $5 \times 5 \,\mu\text{m}^2$ is chosen in the PEEM microscope to accommodate the full model surface with the 16 systems over an area of $3 \times 3 \mu m^2$ in each image, which allows simultaneous measurement for all pairs (Fig. 1f). X-PEEM images are recorded at the range of photon energies 700-718 eV to generate the sequence of the Fe L3 edge XAS spectra (see Supplementary Video), for 453-475 eV for Ti L_{2.3} edge XAS in the case of the titanium oxide support and for 1,550–1,590 eV for Al K edge XAS when the aluminium oxide support is used. X-PEEM is superior to other XAS techniques for measuring the aluminium oxide support since it is a surface-sensitive method, not measuring the bulk, and detects small changes in surface coordination that were identified in previous studies^{27,34}. The series of images in each energy scan are corrected for drift, followed by selection of the desired area on the support or the desired nanoparticle to obtain the spatially resolved individual XAS spectra. Normalization of the spectra is done with a marker that has no absorption edges in the energy range where the XAS spectra are taken. The base pressure of the X-PEEM was around 5×10^{-10} mbar. During hydrogen dosage at 1×10^{-5} mbar and a gradual increase in temperature, dissociation of hydrogen occurs on the platinum nanoparticles, which initiates the spillover effect. Direct reduction of iron oxides to metallic iron(0) in molecular hydrogen occurs only at very high temperature (above 650 K; ref. 35), with no changes in the XAS spectra below 423 K (ref. 14). Therefore, the measurements are performed well below this temperature to account for the partial reduction due only to hydrogen atoms spilling over from platinum.

Alignment of the microscope, stabilization of any drifts in the sample, and obtaining the XAS spectra took an hour at each temperature step, which was kept consistent for both the titanium oxide and the aluminium oxide sample. Beginning at room temperature, the sample temperature was increased in steps of 10 K or 20 K. A crucial balance between the space and time resolution of the X-PEEM microscope and the limits of the dosing under ultrahigh vacuum was maintained. At each temperature, spectra for all 16 iron oxide particles were extracted in the same single measurement to compare exactly the same reaction condition for every pair. Further data analysis and speciation of iron oxide spectra is done using linear combination fitting with the reference of the oxides 14,36 . The XAS spectrum of the native oxide state shows a resonance peak and a shoulder. With reduction of the iron oxide, the intensity of the peak resonance starts to decrease, eventually disappearing when fully reduced^{14,25}, and the shoulder peak intensity increases, eventually to become dominant. Visualization of the whole model system during spectroscopic analysis enables a comparison of the extent of spillover in the different pairs.

From the extent of reduction, it is possible to quantify the percentage of dissociated hydrogen available at different distances from platinum (that is, the concentration gradient). At the experimental stage shown in Fig. 2, all the hydrogen atoms dissociated on platinum in the overlapping pair 'a1' contribute to the reduction of the iron oxide particle, which reduced by 16.8% as determined by linear combination fitting of the iron L3 edge XAS. Iron oxide is reduced by 5%, 2.8% and 1.2% in pairs 'c2', 'c3' and 'c4' respectively. Since the amount of reduction is proportional to the hydrogen atoms used at that particle, using simple proportionality, we calculate the hydrogen concentration available at the iron oxide of each pair in comparison to pair 'a1' (where 16.8% reduction corresponds to 100% hydrogen concentration): in pair 'c2', where the pairs touch each other, it is 29.8%; in pair 'c3', at a distance of $5\,\mathrm{nm},$ it is 16.7%; this drops to as low as 7.1% in pair 'c4', at a distance of $15\,\mathrm{nm}$ from the platinum; and it becomes insignificant as distance increases. Using the results from *in situ* single nanoparticle spectromicroscopy¹⁴ and DFT simulations^{16,17,37,38}, the mechanism of hydrogen spillover in relation to the distance from the platinum catalyst was fully quantified. DFT calculations and the diffusion coefficients corroborate the greater mobility on titanium oxide as compared to undercoordinated Al3c sites in aluminium oxide.

DFT calculations and computational methods. First principles DFT calculations were carried out with the CP2K package (http://www.cp2k.org), based on the hybrid Gaussian and plane-wave scheme^{16,39}. A plane-wave density cutoff of 800 Ry and periodic boundary conditions were adopted. For a better understanding of the semiconductor electronic properties, we used both general gradient approximation and hybrid functionals. General gradient approximation calculations were performed with the Perdew–Burke–Enzerhof (PBE)⁴⁰ exchange correlation functional, while hybrid calculations were carried out with the truncated PBE0 functional^{41,42}, with varying percentages of exact Hartree–Fock exchange, ranging from 25% to 35%. A cutoff radius of 4.5 Å, sufficient to ensure converged electronic

properties in the truncated PBE0 calculations⁴³, was chosen for all calculations with the truncated PBE0 functional. The auxiliary density matrix method, which relies on an auxiliary basis for Hartree–Fock exchange⁴⁴, was used to speed up hybrid calculations. Dispersion interactions were included by means of an empirical analytical potential, using the Grimme D3 method⁴⁵, within a range of 15 Å.

Standard coefficients and scaling factors for PBE and PBE0 functionals were adopted. The primary Gaussian basis set adopted in all calculations is of double ζ quality for all elements, apart from hydrogen (triple ζ quality), in combination with Goedecker-Teter-Hutter pseudopotentials⁴⁶. Validation of the computational setup was carried out for both titanium oxide and aluminium oxide, by comparison with experimental lattice parameters and bond lengths. Differences between computed and experimental parameters were generally less than 1%. Activation energies were computed with the climbing image NEB method^{47,48} with a convergence limit of 2×10^{-5} eV. Density of states analysis was carried out with a resolution of 0.03 eV. The thermodynamically most stable (101) surface was chosen as a model for the anatase titanium oxide interface^{49,50}. The bohemite-based crystal structure of γ -aluminium oxide proposed in ref. 51 and confirmed by theoretical calculations³⁰ was adopted in our model system. Its two most stable surfaces (001) and (100) were investigated and their properties compared. In all modelled slabs, the interface under study was built to be perpendicular to the z axis, facing a vacuum layer about 20 Å thick, whereas the x and y directions are fully periodic.

Hydrogen adsorption and diffusion from DFT. Assessment of the interaction of hydrogen with the anatase and aluminium oxide surfaces is a fundamental step of the investigation. The adsorption energy of a hydrogen molecule on a given surface is computed as:

$$E_{ads,H_2} = E_{2H,surface} - E_{surface,clean} - E_{H_2,vacuum}$$

where $E_{2H, surface}$ is the total energy of the hydrogenated surface, $E_{surface, clean}$ is the total energy of the clean surface, and $E_{H_2, vacuum}$ is the energy of hydrogen in vacuum, not interacting with the surface. Direct comparison to hydrogen in vacuum phase avoids the bias due to the intrinsic instability of a single hydrogen atom in vacuum. The adsorption energy of a single hydrogen atom can then be computed as:

$$E_{ads,H} = \frac{1}{2}E_{ads,H_2}$$

Dissociative hydrogen adsorption on anatase (101) is energetically favourable, and the oxide slab is reduced, with transfer of two electrons to the substrate.

Hydrogen adsorption was investigated on both the (100) and (001) interfaces of γ -aluminium oxide. The process is favourable only at the (100) interface, as it is the one exposing the highly reactive Al3c centres, with an undercoordinated tetrahedral geometry²⁸. On aluminium oxide, hydrogen is heterolytically split, forming a proton and a H⁻ anion, which remain segregated at the interface. Analysis of the spin density distribution and of the system total density of states shows that there is no formation of trap states in the oxide band structure, confirming that no excess electronic density is transferred to the oxide.

Adsorption on a 13-atom platinum cluster (Pt13) was also investigated. Adsorption of the cluster on the oxide was modelled by placing the 13 metal atoms on the surface with three different possible geometries (cuboctahedron and an amorphous two- and three-layered structure) and then letting the system evolve with a molecular dynamics simulation for approximately 5 ps each at 700 K. Cluster geometry samples were obtained at every 1,000th molecular dynamics step, and subsequently the geometry relaxed. The lowest energy cluster geometry was selected as a reasonable approximation for the metal geometry. In agreement with refs 52 and 53, adsorption of a single hydrogen atom on the oxide-supported metal is exothermic, indicating an energetically favourable process. An effect of metal loading, similar to that reported by ref. 54, was also observed: adsorption of a single hydrogen molecule is more favourable on the metal cluster than on the oxide (that is, about -1.5 eV on Pt13 versus about -0.6 eV on titanium oxide). However, the average hydrogen adsorption energy decreases linearly with increasing H coverage of the metal cluster, making hydrogen adsorption on the oxide energetically competitive at the coverage level, which can be predicted under the experimental conditions (that is, about $-0.5\,eV$ on Pt_{13} versus about $-0.5\,eV$ on titanium oxide; for the prediction of coverage, see below). As reported in the main text, we demonstrate that increasing the hydrogen loading of the metal not only affects the adsorption energies, but also significantly lowers the spillover activation energy Eact barriers.

Additional NEB calculations also reveal that hydrogen dissociation on a clear titanium oxide support without any metal particles requires an $E_{\rm act}$ of 2.05 eV, suggesting that titanium oxide is not directly reduced by gas-phase hydrogen (Extended Data Fig. 10a), in agreement with experimental observations (Fig. 3c).

The computed E_{act} for migration of hydrogen atoms on the anatase surface matches well with the value reported by ref. 55, in which computations are carried out at a lower level of theory (general gradient approximation) that does not allow for polaron formation in the oxide. Adopting a higher level of theory proves to be crucial for assessing the role of coadsorbed water molecules on the surface, as their presence could initiate a Grotthus-like charge transfer. The energy barrier associated with the single proton migration decreases from 0.68 eV to 0.15 eV in the presence of a bridging water molecule. On the other hand, when electrons are involved, E_{act} is more or less unaltered, even in the presence of a bridging water molecule (0.71 eV). Electrons migrate within the oxide, from one Ti site to another, without transferring to the water molecule. The migration profile shows a first peak, corresponding to proton transfer between the two neighbouring surface oxygen centres, immediately followed by a barrier-less electron transfer (see also Extended Data Fig. 9). The barrier for migration of the other possible reducing defects in titanium oxide, oxygen vacancies, is much higher ($E_{act} > 1 \text{ eV}$) for 'lateral' migration and therefore formation of Ti³⁺ centres away from the platinum cluster is explained by the migration of the excess electrons that are introduced with oxide hydrogenation. The barrier for subsurface vacancy intercalation (that is, 'vertical' migration) is lower and comparable to hydrogen mobility (0.75 eV), but such migration would result in the defect being more strongly localized below the surface⁵⁶. The mechanism of the mobility of electrons and protons describes the experimentally observed spillover on titanium oxide (Fig. 3). On aluminium oxide³⁰, hydrogen adsorption from the gas phase and dissociation are strongly affected by the presence of co-adsorbed water molecules on the oxide surface, with *E*_{act} ranging from 0.63 eV (dry surface) to 0.99 eV (fully hydrated surface) (Extended Data Fig. 10b). Since water plays an essential role in the stability and reactivity of aluminium oxide^{28,30}, we studied both a hydrated and a dry surface to achieve understanding of the observed distance-dependent mobility of hydrogen atoms on aluminium oxide.

Prediction of surface coverage. In the *ab initio* thermodynamics calculation details, for a given pair of temperature and pressure values (T, p), the most stable surface composition and geometry is the one that minimizes the system free energy $\gamma(T, p)$:

$$\gamma(T,p) = \frac{1}{A} [E_{\text{tot}}^{\text{support},H_2} - E_{\text{tot}}^{\text{support},\text{clean}} - N_{\text{H}}\mu_{\text{H}}(T,p)]$$
$$\mu_{\text{H}}(T,p) = \mu_{\text{H}}(T,p^0) + \frac{1}{2}kT \times \ln\left(\frac{p}{p^0}\right)$$
$$\mu_{\text{H}}(T,p^0) = \frac{1}{2} \{ [H(T,p^0,\text{H}_2) - H(0\text{ K},p^0,\text{H}_2)] - T[S(T,p^0,\text{H}_2) - S(0\text{ K},p^0,\text{H}_2)] \}$$

where *A* is surface area, E_{tot} is the total energy, p^0 is standard pressure (1 bar), *H* is enthalpy, *S* is entropy and $\mu_i(T, p)$ is the chemical potential of species *i*, at given temperature and pressure. The parameter $\mu_i(T, p)$ includes the vibrational, rotational and ideal gas entropy contributions to the chemical potential of the species *i*. The computed values for hydrogen $\mu_H(T, p^0)$ at the given temperatures are: -0.03 eV (at 50 K); -0.08 eV (at 100 K); -0.14 eV (150 K); -0.20 eV (at 200 K); -0.26 eV (at 200 K); -0.56 eV (at 450 K); -0.63 eV (at 500 K); -0.71 eV (at 550 K); -0.79 eV (at 600 K); -0.88 eV (at 650 K); -0.96 eV (at 700 K); -1.04 eV (at 750 K); -1.13 eV (at 800 K) and -1.21 eV (at 850 K).

Calculation of diffusion coefficients. Diffusion on a surface depends not only on the activation energy for the movement of an atom on a surface but also on the availability of neighbouring sites and on the temperature of the system. The mobility of a surface adsorbed atom is therefore better represented by the diffusion coefficient, *D*.

A first approach to the problem of surface diffusion is the random walk model proposed by A. Einstein⁵⁷. It involves modelling the motion of individual particles as random walks in the same way as the motions of gas molecules are modelled. According to the random walk model for diffusion, the macroscopic surface diffusion coefficient *D* for an atom (or molecule) on a two-dimensional surface can be computed by the following expression⁵⁸:

$$D = \frac{\langle \Delta r^2 \rangle}{zt} = \frac{\nu a^2}{z}$$

where $\langle \Delta r^2 \rangle = \nu a^2 t$ is the mean square displacement at time *t*, *a* is the distance travelled by the atom in a single hop (the spacing between adsorption sites), and ν is the microscopic jump frequency. *z* is the number of neighbouring sites to which

the atom can hop. For one-dimensional diffusion, that is, when the atom can hop either to the left or to the right neighbouring site, as is the case for titanium oxide and γ -aluminium oxide, z = 2.

The harmonic transition state theory model relates the microscopic jump frequency to the activation energy E_{act} for surface diffusion and to the temperature, as shown in the following expression:

$$\nu = \nu_0 \exp\!\left(\frac{-E_{\rm act}}{kT}\right)$$

where ν_0 is the attempt frequency required to overcome the activation energy barrier, *T* is temperature and *k* is Boltzmann's constant.

The harmonic transition state theory model is a good approximation for many solid-state and surface reactions, because the energy barriers are often large compared to the average kinetic energy in the system, kT. This is important because it ensures that the system reaches a local equilibrium between reactive events. ν_0 can be obtained by considering the nature of the state where the atom is between the lattice sites (saddle point).

NEB optimization was performed in such a way that one of the images converges to a saddle point (as opposed to all the images being evenly spaced along the reaction coordinate). This is called climbing-image NEB; an optimized climbing-image NEB has a saddle point as its highest energy image⁴⁸. The attempt frequency will be given by the frequency at which the atom in the saddle point will vibrate along the reaction path and can be computed by:

$$\nu_0 = \frac{\prod_i^{3N} \nu_i^{\mathsf{R}}}{\prod_i^{3N-1} \nu_i^{\mathsf{S}}}$$

where N is the total number of atoms, and ν_i^{R} and ν_i^{S} are the normal mode frequencies at the reactant and saddle point. There is exactly one imaginary frequency at the saddle point, giving the index 3N-1.

The activation energy $E_{\rm act}$ is defined as the difference in energy between the saddle and reactant energy. The exponential term represents the Boltzmann probability that a vibrational along the reaction direction will overcome the barrier and continue into the product state.

For hydrogen diffusion on titanium oxide, the computed value of the attempt frequency is 3,646 cm⁻¹, the activation energy barrier is 0.73 eV (independent of water coverage) and the diffusion coefficient at 300 K is 4.15×10^{-14} cm² s⁻¹. For hydrogen diffusion on aluminium oxide, the respective values are 1,938 cm⁻¹, 1.32 eV (intermediate water coverage) and 1.39×10^{-23} cm² s⁻¹.

Data availability. The data that support the findings of this study are available from the authors on reasonable request.

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(green) have a diameter of 30 nm. The distance between the dimeric pairs is 1 μ m. **b**, SEM image of the nanofabricated model system on titanium oxide support (5 nm thick) which is an exact one-to-one rendition of the design (500 nm scale bar). **c**, Scheme of different stages of overlaid EBL to fabricate the model system (details in Methods).



Extended Data Figure 2 | **Initial state of iron oxide particles on the aluminium oxide support.** Fe L₃ edge XAS spectra of the iron nanoparticles at room temperature in pair 'a1' (overlapping pair), pair 'c2' (just touching each other), pair 'd3' (45 nm distance) and system 'd4', which has no platinum in its vicinity. All the iron nanoparticles have the same initial state, which is the native oxide, formed by exposure of iron particles in air after nanofabrication. Iron oxidation occurs through initial

formation of iron(II) oxide followed by progressive transformation to iron(II,III) oxide. A small amount of iron(II) oxide remains owing to its limited oxidation at the interface^{14,36}. The XAS spectrum of the native oxide state shows a resonance peak and a shoulder. With reduction of the iron oxide, the peak resonance starts to decrease and the shoulder peak intensity increases¹⁴.



Extended Data Figure 3 | **Speciation of iron oxide particles on aluminium oxide in the 16 systems at 343 K.** The fits are extracted using linear combination fitting of the experimental XAS spectra with the reference of metallic iron(0), iron(II) oxide, iron(II,III) oxide, and iron(III) oxide^{14,36}. The Fe L₃ edge XAS spectra in Fig. 2a shows higher reduction for the iron oxide particles at distances less than 15 nm from the platinum particles, that is, in pairs 'a1' to 'c4'. The initial state was iron(II,III) oxide and iron (II) oxide (Extended Data Fig. 2). During reduction, the fraction of iron(II,III) oxide decreases and that of iron (II) oxide increases. A decrease in the fraction of iron(II) oxide on further reduction results in the evolution of metallic iron(0). The pair with overlapping iron oxide and platinum particles (pair 'a1') is most reduced, producing 16.8% of iron(0). The extent of reduction decreases as the distance between the particles increases in each following pair. The iron oxide particle in pair 'c4' (with an interparticle distance of 15 nm) has 1.2% of iron(0) and the iron oxide particles in pairs 'd1', 'd2' and 'd3' and system 'd4', at distances more than 15 nm from their corresponding platinum particles, have no iron(0). This shows the gradient of reduction depending on the distance from the platinum catalyst up to 15 nm.



Extended Data Figure 4 | Evidence of three-coordinated surface aluminium sites on aluminium oxide. a, Al K edge XAS spectra of the aluminium oxide support at around 300 K and 10^{-10} mbar without hydrogen. The absorption edge observed in the measured spectra at 1,566 eV and the characteristic broad peak at about 20 eV indicate a dominant tetrahedral aluminium coordination. An increase in intensity in the range 1,567–1,575 eV is visible, along with the lower white line intensity and the lower intensity of the broad peak at 1,583 eV compared to purely tetrahedral aluminium coordination: this is indicative of a small amount of octahedrally coordinated aluminium at the cost of tetrahedrally

coordinated aluminium³⁴. The visible pre-edge feature is characteristic of three-coordinated aluminium sites (Al3c)²⁷, which confirms their existence under the experimental conditions. At higher water coverage, these Al3c sites are known to be unavailable²⁸, which will lead to the disappearance of this pre-edge feature. **b**, Calculated thermodynamic diagram showing that the availability of Al3c sites depends on the partial pressure of water $p_{\rm H_2O}$ in the system. Coloured areas indicate the percentage of free Al sites on the surface for a given value of temperature and $p_{\rm H_2O}$.



Extended Data Figure 5 | **Uniform reduction in all pairs on titanium oxide support.** Fe L₃ edge XAS spectra of the single iron oxide particle on the titanium oxide support, without any platinum (particle 'd4' in Extended Fig. 1a) compared with the overlapping pair (pair 'a1') and the pair with interparticle distance 45 nm (pair 'd3') at different stages of reduction: **a**, Initial state at room temperature; **b**, at 343 K; and **c**, at 353 K. All the iron oxide particles are equally reduced irrespective of the distance from platinum.



Extended Data Figure 6 | Speciation of iron oxide particles on titanium oxide at different temperatures. Fits are extracted using linear combination fitting of the experimental XAS spectra with the reference of metallic iron(0), iron (II) oxide, iron(II,III) oxide, and iron(III) oxide^{14,36}. The XAS spectra of all 16 iron oxide nanoparticles on titanium oxide coincide at all temperatures (Extended Data Fig. 5). The iron–iron oxide core–shell particles have multilayered scales of iron(0), iron (II) oxide, iron(II,III) oxide and iron(III) oxide at the native oxide stage at 298 K. With hydrogen dosage of 1×10^{-5} mbar, the particles start to

reduce as temperature is increased leading to interconversion of oxides and evolution of a metallic iron core. Initial reduction of the outermost shells of iron(III) oxide and iron(II,III) oxide leads to an increase in concentration of iron(II) oxide, some of which reduces to metallic iron. The concentration of metallic iron, signifying the extent of reduction at each stage, increases further as iron(II) oxide reduces and the iron(III) oxide is negligible. 17% of iron(0) is seen at 343 K for all iron particles, which increases to 33.6% at 353 K as the particles reduce further.



Extended Data Figure 7 | **Ti L**_{2,3} **edge XAS spectra of the titanium oxide support.** Spectra are taken at each of the pairs, at the lone iron oxide particle and in an isolated area on the surface at least 1 µm from any platinum or iron oxide particles at different temperatures: **a**, 300 K;

b, 323 K; c, 343 K; and d, 353 K. Reduction of titanium oxide occurs uniformly all over the surface, irrespective of the distance from platinum. The rapid diffusion of H atoms results in a range much larger than $1\,\mu m$ for the reduction of the surface.



Extended Data Figure 8 | **Calculated thermodynamic diagrams. a**, The most stable hydrogen coverage of a Pt₁₃ cluster supported on anatase, as a function of temperature and partial hydrogen pressure $p_{\rm H_2}$. Hydrogen adsorption on the metal becomes less favourable with increasing temperature and decreasing $p_{\rm H_2}$. The average number of hydrogen atoms per Pt cluster is indicated by coloured lines. They are indicative only, because of the multitude of possible hydrogen and platinum configurations. The experimental conditions correspond to a coverage between 28 and 18 H atoms on a Pt₁₃ cluster, yielding an estimated H:Pt

ratio between 1.15 and 2.38 under the experimental conditions. **b**, The most stable coverage of the anatase (101) surface at 350 K, as a function of $p_{\rm H_2}$ and $p_{\rm H_20}$. Hydrogen and water adsorb on two different sites on anatase, so that a mixed H₂/H₂O coverage is possible for a relatively wide range of $p_{\rm H_2}$ and $p_{\rm H_20}$ (green–yellow–orange areas in the graph). The percentage coverage indicated in the legend refer to the percentage of occupied two-coordinated oxygen (O_{2c}) sites (H adsorption) and the occupied five-coordinated titanium (Ti_{5c}) sites (H₂O adsorption), respectively.



Extended Data Figure 9 | **Computation of activation energy profiles on titanium oxide.** a, E_{act} profiles computed with the NEB method for migration of hydrogen atoms on the anatase surface in presence (blue) or absence (red) of a neighbouring water molecule, acting as a bridge between sites. b, Comparison of activation energies for proton migration (green) and hydrogen migration (blue) via a bridging water molecule. Proton migration in the absence of water is also reported (black). **c**, Ball-and-stick model of the oxide surface with co-adsorbates, describing the

molecular parameters used to compute the reaction coordinate. Colour coding: red, O; yellow, H; silver, Ti. The blue density surface represents a localized electron in a filled Ti 3*d* orbital. The reaction coordinate without water mediation is computed as the combination of interatomic distances, $d_{O_1-H_1} - d_{H_1-O_2}$. The reaction coordinate with water mediation is computed as $d_{O_1-H_1} - d_{H_2-O_2}$. When water molecules are present on the surface, the distances between surface hydrogen atoms and the neighbouring water molecules are also reported: 2.14 Å and 2.34 Å.



Extended Data Figure 10 | Illustration of the most relevant mechanisms of hydrogen adsorption and migration on titanium oxide (101) and γ -aluminium oxide (100), computed by the NEB method. The results corroborate experimental observations. All energies are normalized to the energy of the isolated hydrogen molecule in the gas phase. Colour coding in the ball-and-stick models: red, O; yellow, H; silver, Ti; blue, Pt; and cyan, Al. Filled Ti 3*d* orbitals are indicated by a blue density surface.

In each of the two surface models the main stages of hydrogen adsorption are illustrated. A is the gas-phase hydrogen molecule; B is a hydrogen molecule weakly interacting with the oxide surface (physisorption); and C is a hydrogen molecule dissociatively adsorbed on the oxide surface. **a**, Hydrogen dissociation on clean anatase titanium oxide: $E_{act} = 2.05 \text{ eV}$. **b**, Hydrogen dissociation on γ -aluminium oxide: $E_{act} = 0.63 \text{ eV}$ on the clean surface (red) and $E_{act} = 0.99 \text{ eV}$ on the hydrated surface (blue).