Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

for Ms

Molybdena Deposited on Titania by Equilibrium Deposition Filtration: Evolution of the Structural Configuration of Oxo-Molybdenum (VI) Sites with Temperature

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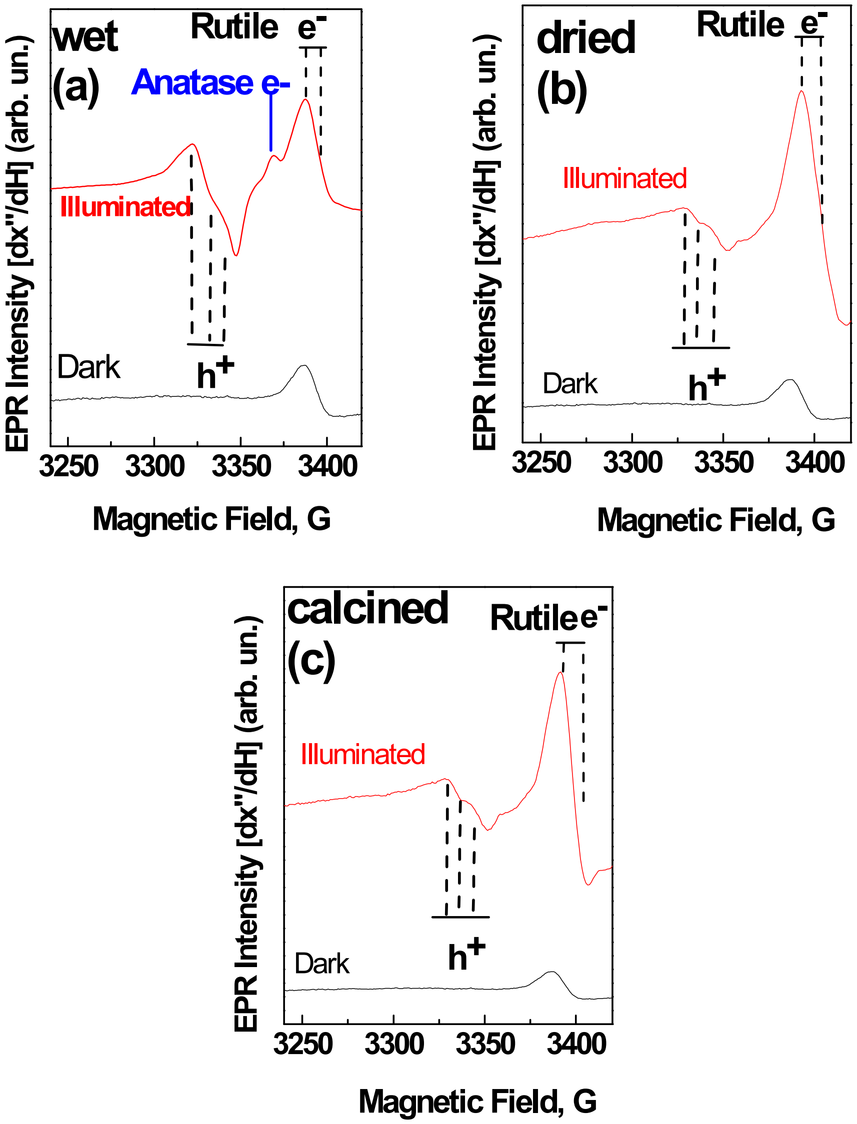

Figure S1. EPR spectra for reference TiO_2/P25 samples. Black lines: dark; red lines: illuminated samples. (a) wet sample; (b) dried sample; and (c) calcined sample. In (a), the blue arrow marks the position where the lattice electrons from anatase phase are expected to show up.[46]

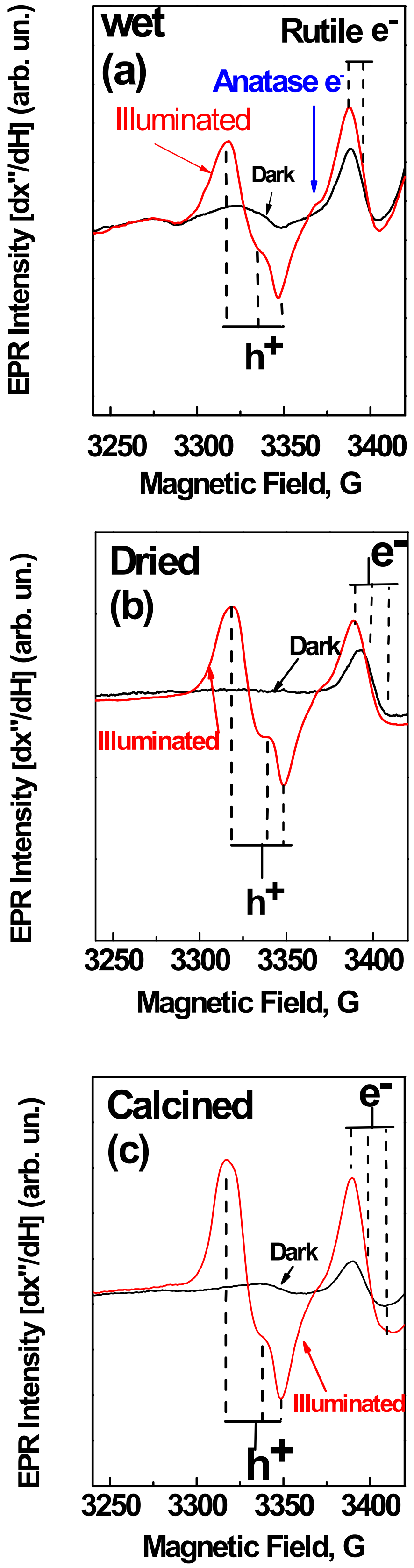

Figure S2. EPR spectra for 2.6MoTi samples. Black lines: dark; red lines: illuminated samples. (a) wet sample; (b) dried sample; and (c) calcined sample. In (a), the blue arrow marks the position where the lattice electrons from anatase phase are expected to show up.[46]

In the wet sample, anatase and rutile electrons are photoinduced,[43] together with a considerable amount of h^+ centers[44,S1]. It is well known that anatase is the photoactive phase that transfers rapidly electrons on the surface, *i.e.* that in turn would interact with surface bound species such as Mo^{6+} to reduce it to Mo^{5+}. It is also well known that rutile serves to optimize the e^-/h^+ separation, decreasing the recombination rate. This has been amply analyzed in ref. 41 as well as in ref. S1. The e-transfer activity of rutile is inferior than anatase's.

Thus in the present work, the relative intensities of these e^- and h^+ signals should be viewed through a mutual e^-/h^+ balance[41, S1]: processes that quench electrons would result in increased h^+ signals and *vice-versa*.

Indeed, in the present study we observed two interrelated phenomena: (*i*) the electrons of anatase are rapidly transferred to the Mo-species forming Mo^{5+}; (*ii*) the anatase holes are increased in the presence of Mo. Tighter association of Mo on TiO_2, for example in the 450^0C-treated sample increases the holes due to e-tranfer to Mo-species. In contrast, in the reference TiO_2/P25 (without deposited Mo-oxo species) calcination at 450^0C had the opposite effect, *i.e.* enhancing the electrons and suppressing the holes. In all cases electrons in rutile are inactive thus they show up with considerable intensity, however these are non-reactive, *i.e.* they cannot be transferred to Mo-species. This is why rutile-electrons are always present in all samples.

References

S1. D. C. Hurum, A. G. Agrios, K. A. Gray, T. Rajh and M. C. Thurnauer, *J. Phys. Chem. B*, 2003, **107**, 4545.
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