

Experimental Report

Proposal CH-468

***In situ* investigations of the active state of Rh co-catalysts on semiconductors during photocatalytic H₂ production via overall water splitting and selective oxidation**

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A) Abstract

The electronic state of noble-metal co-catalysts on semiconductor photoabsorbers relevant for photocatalytic H₂ generation *via* either overall water splitting ($2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$) or photoreforming of oxygenated hydrocarbons (e.g., $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$) was investigated by means of *in situ* XANES measurements in liquid reaction media. XAFS measurements were performed on Rh-, Pt- and Pd-decorated TiO₂ (1 wt.% noble metal loading) photocatalysts for photoreforming and on Rh- and Pt- decorated SrTiO₃ semiconductors (0.1-1 wt.% noble metal loading), which are active in anodic O₂-evolution from water, and thus enable photocatalytic overall water splitting. In addition, a Rh-decorated SrTiO₃ co-modified with a hydrated CrO_x-shell was examined. The latter is mandatory to achieve water splitting as it acts as a molecular sieve under reaction conditions preventing O₂-adsorption and back-reaction to water ($\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$). Preventing the back reaction enables efficient H₂-generation from water in absence of sacrificial agents. The results obtained at ESRF ID26 demonstrate that noble metals, independently of the as-prepared state, reduce *in situ* to the metallic state, which constitutes the active state under H₂-evolution conditions. In pure H₂O and in the absence of illumination, the co-catalysts remain mainly oxidized due to air exposure after preparation. We could show that upon band gap irradiation, reduction to the metals occurs *in situ* in pure water. In contrast, under photoreforming conditions (in the presence of aqueous glycerol or methanol) we encountered reduction to the metals already under dark conditions in the presence of the oxygenate indicating that the latter acted as a reducing agent to the co-catalysts at ambient conditions. The combination of low co-catalysts loadings (0.1 wt.% Rh) and strongly competing Sr-fluorescence at the Rh K-edge excitation energies did not allow for examination of the Rh-decorated SrTiO₃ samples. It is planned to complete these investigations in the future. These findings contribute to a better understanding of the role of the co-catalyst on the photocatalytic activity of solid semiconductors.

B) Potential publication

During a preliminary experimental run at ESRF BM25 we were able to acquire a first dataset characterizing Rh/TiO₂ and Rh/GaN:ZnO photocatalysts *ex situ*. We published this data in the context of a kinetic/mechanistic investigation of photoreforming (T.F. Berto, K.E. Sanwald, W. Eisenreich, O.Y. Gutiérrez, J.A. Lercher, J. Catal. 338 (2016)). The spectra obtained at ESRF ID26 are fully evaluated and analyzed and will be included in further manuscripts that are currently in preparation. Therein, the *in situ* XANES measurements are indispensable in understanding the impact of the co-catalysts in relation to the kinetic experiments performed at our home institution. Further oral contributions to international conferences are planned and in preparation.

C) Experimental results

We discuss the electronic state of the noble metal (Rh, Pd, Pt) co-catalyst decorating TiO₂. The metal nanoparticles (typically 1 wt.% of metal) were loaded on TiO₂ *via* incipient wetness impregnation of a precursor solution followed by thermal treatments in synthetic air and H₂. The resulting materials were examined by a series of standard techniques available at

Technische Universität München (XRD, TEM, N₂ and H₂ sorption). Exemplarily, spectra at the Rh K-edge recorded under dry (as-prepared and after thermal reduction in H₂ at 250 °C) and liquid-phase conditions (ambient, anaerobic environment) relevant to photocatalytic H₂-generation are depicted in Fig. 1. Reference spectra are shown for comparison (Fig. 1 (A)). Rh existed predominantly in its oxidic state in the dry catalyst, as deduced from the similarity of the catalyst to the spectrum of Rh₂O₃. This is likely due to re-oxidation of the nanoparticles upon exposure to air after preparation. As a further reference, complete reduction to the metal may be achieved upon treatment in H₂ (Fig. 1 (B)). Rh in the as-prepared photocatalyst retained its oxidic nature upon immersion in liquid H₂O. However, upon irradiation with UV-Vis illumination for about 30 minutes, the transformation to metallic Rh was readily observed (Fig. 1 (C)). This shows that metal is the photocatalytically active state. As the H₂-evolution activities of TiO₂-based photocatalysts in pure H₂O (in the absence of oxygenated hydrocarbons) are very poor, the reduction of Rh oxide species upon illumination indicates that co-catalyst reduction originates directly from photogenerated electrons rather than from evolved H₂. Contrarily, complete reduction of RhO_x was observed already before UV-Vis irradiation in presence of glycerol (Fig. 1(D)) indicating that the oxygenate acts as reducing agent under these conditions. Similar findings were obtained by application of an aqueous methanol solution or when omitting the H₂-reduction step during catalyst preparation. In the presence of oxygenated hydrocarbons, XANES remained mainly unchanged after provision of UV-Vis irradiation. Regarding the state of the co-catalyst, equivalent findings were obtained in case of Pt and Pd co-catalysts which demonstrate the generality and validity of the findings for noble metals.

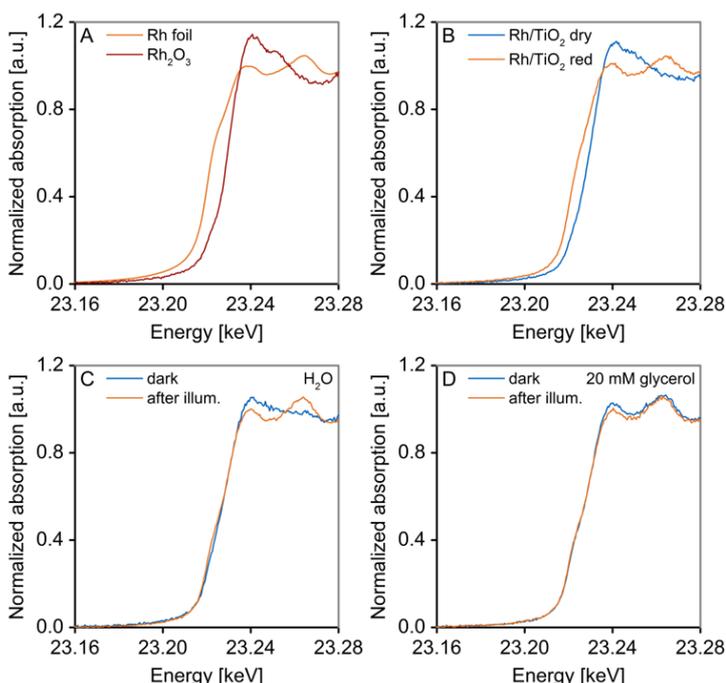


Fig. 1 Rh K-edge XANES of 1wt.% RhO_x/TiO₂ recorded under different conditions. (A) References compounds. (B) Catalyst in dry state and after reduction in H₂. Catalyst in (C) liquid H₂O and (D) 20 mM aqueous glycerol before/after UV-Vis.

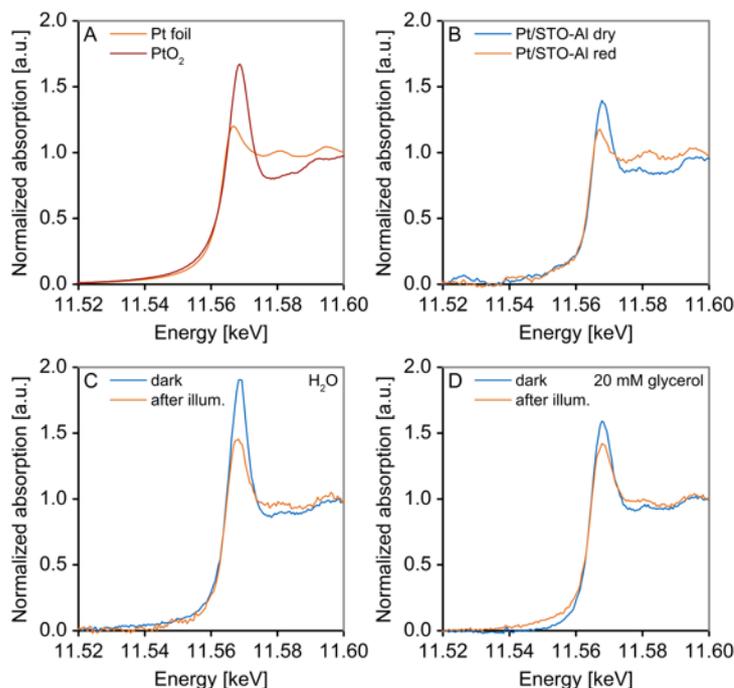


Fig. 2 Pt L3-edge XANES of 0.1wt.% PtO_x/SrTiO₃ recorded under different conditions. (A) References compounds. (B) Catalyst in dry state and after reduction in H₂. Catalyst in (C) liquid H₂O and (D) 20 mM aqueous glycerol before/after UV-Vis.

A more complex scenario may arise when the semiconductor is active in water oxidation, e.g. SrTiO₃. In this case, evolved O₂ or surface oxidizing species have the potential to oxidize the metal. In turn, the performance and role of the co-catalyst might change with the oxidation state. However, in the exemplary case of Pt/SrTiO₃ (Fig. 2), the oxidized state of the co-catalysts (reached during air exposure) fully transforms to metal in the presence of oxygenates or under illumination. Therefore, the activity for water oxidation at the anode did not significantly influence the state of the co-catalyst.

We furthermore recorded *in situ* XANES of a core-shell type RhCrO_x/SrTiO₃ photocatalyst (Fig. 3), where the chromia shell was deposited *via* photoreduction of a Cr(VI) precursor (K₂CrO₄). Missing the pre-edge feature in the sample spectra clearly provides evidence of the absence of Cr(VI) and formation of an oxidic Cr(III) shell. The state of the latter remained unchanged in different reaction media as well as before/after UV-Vis irradiation. The pronounced differences encountered comparing the XANES of the photocatalyst samples to a dry Cr₂O₃ reference are attributed to the formation of a hydrated Cr(III)oxyhydroxide (Cr(III)O_x(OH)_y · z H₂O) which is expected to provide H⁺-conductivity and H₂-diffusivity at the cathode under H₂-evolution conditions.

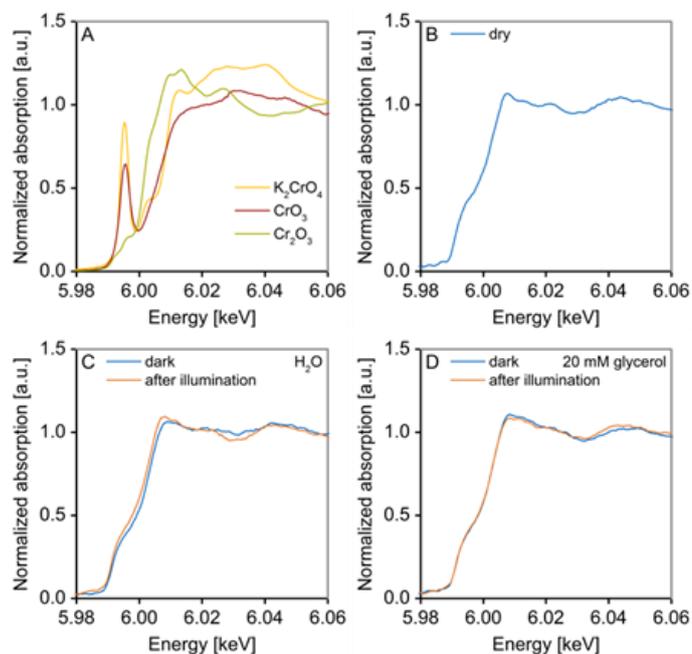


Fig. 3 Cr K-edge XANES of RhCrO_x/SrTiO₃ (0.1 wt.% Cr) recorded under different conditions. (A) Reference compounds. (B) Catalyst in dry state. Catalyst in (C) liquid H₂O and (D) 20 mM aqueous glycerol before/after UV-Vis.