Photocatalytic hydrogen production over ultradispersed Pt/TiO_2 catalysts

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Abstract: Photocatalytic hydrogen production is an active research field since "solar hydrogen" could be used as a renewable fuel in the future. Such a challenging target requires rationally designed metal/semiconductor photocatalysts. To this aim, recently developed "single-atom catalysts" (SACs) and more generally ultradispersed catalysts, are promising candidates. Herein, we show that Pt/TiO_2 SACs are as efficient as reference Pt nanoparticle (size > 2 nm) catalysts in photocatalytic ethanol dehydrogenation but twice less than their Pt cluster counterparts (size 1 nm). Unlike Pt dispersion, controlling the titania morphology did not allow us to enhance hydrogen production activity with respect to commercial titania.

Keywords: Photocatalytic hydrogen production, Single-atom catalysts, Shape-controlled titania.

1. Introduction

Sustainable production of hydrogen from renewables (water, biomass, sunlight, etc.) is of worldwide interest because H_2 can be used as a versatile energy carrier, e.g. in fuel cells. Among the possible routes, photocatalytic hydrogen production from biosourced alcohol (e.g. methanol or ethanol) dehydrogenation is the most promising.[1] This reaction makes use of metal/semiconductor bifunctional photocatalysts such as the prototypical Pt/TiO_2 system. The role of Pt, which is generally in the form of nanoparticles (size ≥ 2 nm), is to enhance photogenerated electron-hole pair separation to facilitate the reduction of protons issuing from the dissociative adsorption of the alcohol at the titania surface.

It is supposed that the dimensionality of the metal particles and their interaction with the semiconducting support strongly influence electron capture and H-H recombination into H_2, i.e. the efficiency of the whole process. However, these effects have been scarcely investigated. Besides, noble metals highly dispersed on oxide supports, in the form of single atoms up to small clusters (size < 2 nm), are currently emerging as a new generation of catalysts.[2]

2. Experimental

Ultradispersed 0.2 wt% Pt/TiO_2 photocatalysts were prepared by standard impregnation/post-treatment methods using $Pt(NH_3)_4(NO_3)_2$ and various phases of titania: commercial anatase-rutile mixture (Degussa P90, 114 m^2/g) and phase/shape-controlled nano-objects (e.g. anatase nanowires, Fig.1a) synthesized by hydrothermal methods.

The materials were characterized by a variety of techniques including aberration-corrected scanning transmission electron microscopy (STEM-HAADF). The photocatalytic hydrogen generation performances were evaluated for the dehydrogenation of ethanol in a gas-phase flow reactor using a 365 nm UV diode.

3. Results and discussion

Well-defined Pt/TiO_2 catalysts containing, depending on the thermochemical post-treatment, either single Pt atoms or Pt clusters (size < 2 nm), have been successfully prepared. As a result, the 0.2 wt% Pt/TiO_2-P90 single-atom catalyst appears as active as a reference 1 wt% Pt/TiO_2-P25 nanoparticulate catalyst prepared by photodeposition (NP REF in Fig. 1b), while 1 nm-sized Pt clusters supported on TiO_2-P90 are nearly twice more active.

The performance of shape-controlled catalysts is lower and appears strongly related to the nature of the titania phase, anatase being more active than rutile and B polymorphs.

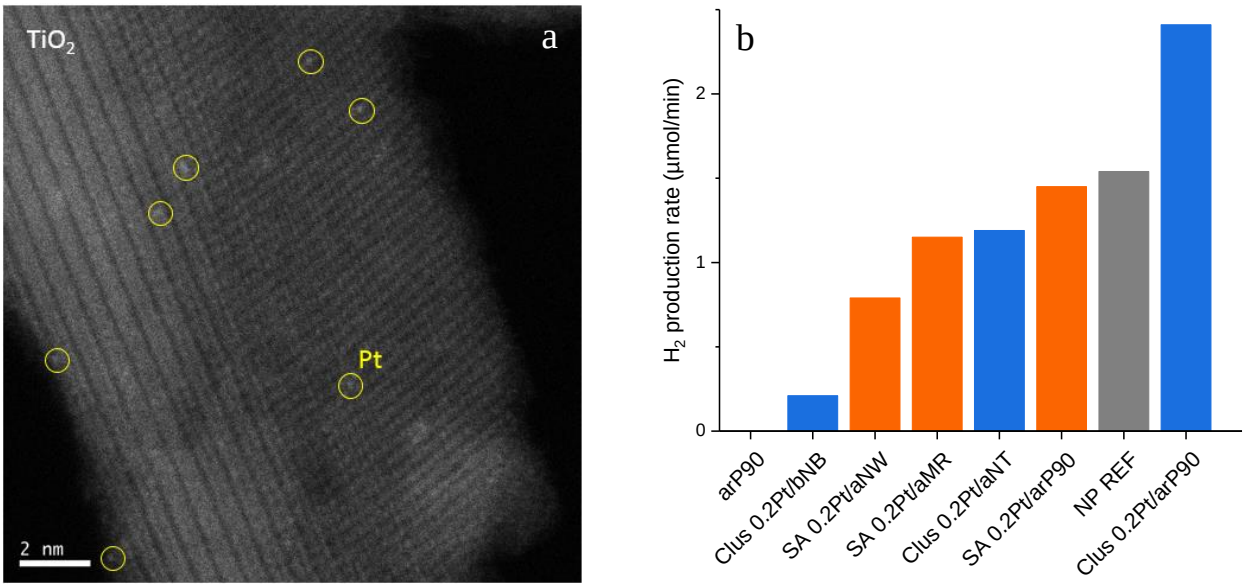

Figure 1. (a) STEM-HAADF image of Pt single atoms supported on anatase TiO_2 nanowires. (b) Comparison of photocatalytic H_2 production activities after 1 h on stream. SAC, Clus and NP stand for Pt single atoms (orange bars), clusters (blue bars) and nanoparticles (grey bar), respectively. The letters a, r and b correspond to anatase, rutile and B TiO_2 phases, respectively. NB, NW, MR and NT stand for nanobelts, nanowires, microrods and nanotubes, respectively.

Post-reaction STEM analyses show that some part of the initially single Pt atoms aggregate into clusters during the photocatalytic reaction. However, surprisingly, their steady-state activity is always lower than that of the cluster catalysts. Forthcoming *operando* photocatalytic X-ray absorption spectroscopy (XANES/EXAFS) investigations will help us to explain these findings and relate the Pt dispersion and oxidation state to the photocatalytic performance.

4. Conclusions

Ultradispersed Pt/TiO_2 photocatalysts with variable Pt particle size and titania phase/morphology have been synthesized by hydrothermal and impregnation methods. The catalytic performances have been compared in the photocatalytic dehydrogenation of ethanol. In combination with commercial anatase-rutile titania, 1 nm Pt clusters appear more efficient than larger Pt particles and single Pt atoms.

References

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