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***In situ* attenuated total reflection infrared spectroscopy study of the photocatalytic steam reforming of methanol on Pt/TiO₂**

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ABSTRACT

The effect of Pt deposition on TiO₂ and of Pt particle size on the photocatalytic steam reforming of methanol was studied by *in-situ* attenuated total reflectance infrared spectroscopy (ATR-IR). Two 0.5 wt.% Pt/TiO₂ samples were investigated, one possessing Pt nanoparticles of *ca.* 4 nm mean size, the other Pt clusters of *ca.* 1.3 nm mean size showing significantly different photoactivity in terms of both hydrogen production rate and selectivity to CO, CO₂ and all other by-products. The presence of Pt nanoparticles strongly affects both the adsorption/desorption and the reactivity properties of the TiO₂ surface. Moreover, the variation of the IR spectrum background upon UV-vis irradiation proved that the photopromoted electrons can be trapped by the Pt particles with the consequent increasing of electron-hole separation. Reducing the Pt size from nanoparticles to clusters increases the rate of methanol and water absorption and hinders the detrimental formation of irreversibly adsorbed CO on Pt. All of these aspects contribute to increase the photocatalytic performance of Pt cluster-decorated TiO₂ with respect to Pt nanoparticles containing TiO₂. Finally, prolonged exposure of all samples to methanol/water vapour in the dark led to the formation of unreactive formate which persists also under UV-vis irradiation. By contrast, this spectator species does not form when the sample is exposed to methanol/water vapour under UV-vis irradiation.

Keywords: Photocatalytic hydrogen production, *in situ* ATR-IR, flame spray pyrolysis, Pt clusters

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