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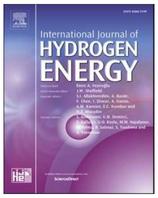

Evolution of atomically dispersed co-catalysts during solar or UV photocatalysis for efficient and sustained H_2 production

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ABSTRACT

The evolution of metal/titania photocatalysts during photocatalytic H_2 evolution is herein studied. Samples containing atomically dispersed Pt co-catalysts (single atoms, clusters and sub-nanoparticles) formed after calcination were compared to pre-reduced analogues mostly having metallic nanoparticles (diameters >1 nm) during ethanol photoreforming under either UV-rich irradiation or natural sunlight. Aggregation of ultra-dispersed oxidised platinum entities ($Pt^{\delta+}$) with concomitant reduction into Pt^0 nanoparticles (1–2 nm) was observed after UV irradiation by transmission electron microscopy (TEM), and diffuse reflectance UV–visible (DRUV-vis) and X-ray photoelectron (XPS) spectroscopies. A parallel, albeit slower, evolution trend was evidenced during solar photocatalysis. Conversely, atomically dispersed Cu co-catalyst species did not grow and became *in-situ* reduced into sub-nanometric Cu^0 under irradiation. Hydrogen production rates were remarkably high during initial stages of UV irradiation, and then declined to a sustained regime (≈50 and 8 mmol g^{-1} h^{-1} for Pt/TiO_2 or Cu/TiO_2, respectively, for up to 24 h of irradiation). Steadier solar photoreforming was observed in experiments performed in a compound parabolic collector tubular reactor (≈7.6 and 1.7 mmol g^{-1} h^{-1} for Pt/TiO_2 or Cu/TiO_2, respectively). Despite the non-negligible effect of co-catalyst rearrangement on activity rationalised herein, attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy measurements pre- and post-photocatalysis suggest that accumulation of strongly adsorbed degradation intermediates, chiefly acetate, is a major cause for rate decreases. Notwithstanding, this phenomenon did not result in total deactivation, so that sustained hydrogen production upon long-term irradiation was not compromised.

1. Introduction

The sustainability of energy and chemical industry in terms of supply security and climate change mitigation is a matter of serious concern. The use of hydrogen is being proposed as one of possible solutions to, on the one hand, overcome the excessive reliance on fossil fuel resources, and in turn, reduce global carbon dioxide emissions [1,2]. Hydrogen may become a clean and renewable energy carrier for transportation, energy supply and, moreover, as an industrial commodity [3]. Regrettably, its current uses are restricted to traditional (petro)chemical processes, chiefly crude oil refining or ammonia production [4]. Low-emissions, renewable, green hydrogen produced by electrolysis of water still represents a minor fraction (*ca.* 0.1%) of global production despite the social and political momentum it is gaining [4]. Valorisation of biomass or waste feedstocks represents an alternative option for the production of hydrogen [5]. Most of these latter routes are performed via high-temperature processes such as gasification of raw solid substrates [6,7] or by catalytic reforming of pre-processed feedstocks [7,8]. The use of sunlight energy to directly drive hydrogen production is an emerging approach [9], embodied in two main solar technologies: overall water splitting [10–12] and reforming of renewable carbon feedstocks such as biomass or solid waste [13–16]. Such processes take place under remarkably mild conditions, namely near-ambient temperature and pressure, with minimal energy input other than sunlight [13,15,17].

Photocatalytic hydrogen production from organic substances in aqueous environments, *i.e.* photoreforming, entails anaerobic degradation essentially employing only water as the oxidising agent [15]. It often proceeds at higher photonic quantum yields than overall water splitting, owing to more favourable thermodynamics [15,18]. If

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