



Photocatalytic methanol assisted production of hydrogen with simultaneous degradation of methyl orange

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ABSTRACT

Platinized TiO₂ prepared by photodeposition was evaluated for activity in the simultaneous conversion of methyl orange (MO), and methanol assisted formation of hydrogen. Low concentrations of MO were found ineffective for generation of hydrogen in measurable quantities upon illumination of Pt/TiO₂ in water. On the other hand, methanol induced hydrogen formation was significant. Surprisingly, when methyl orange was added to the methanol/water solution, hydrogen formation was significantly suppressed. The origin of this detrimental effect of methyl orange lies in the strong and preferred adsorption of the dye on the Pt sites of the catalyst, resulting in hydrogenation of the azo bond and suppression of the catalyzed formation of hydrogen. The hydrogenation of the azo bond is corroborated by dis-colorization of the solution and the observation of a mass fragment in LC-MS analysis corresponding to a hydrogenated product of MO ($m/z = 172$). Similar to hydrogen formation, dye dis-colorization is stimulated by the presence of methanol, without the formation of new chemical compounds, confirming the role of methanol as a hole scavenger in the photocatalytic processes. Finally the presence of oxygen (in lean conditions) delays dye hydrogenation and hydrogen formation, which we discuss is due to oxygen adsorption and formation of superoxide anions over the Pt sites (leading to oxidation of methanol), which is preferred over N=N bond hydrogenation, and proton reduction.

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1. Introduction

Potable water in several domestic areas not only contains organic toxins, but also significant amounts of nitrate, which both have adverse effects on human health [1,2]. To mitigate these issues, photocatalysis is a promising technology, in particular if oxidation of organic toxins to CO₂ [3,4], could be combined with the in situ generation of hydrogen [5,6], needed for reductive elimination of nitrate by heterogeneous catalysis [7]. Both reactions (generation of hydrogen, and reductive elimination of nitrates) could e.g. be performed sequentially in domestic appliances, designed on the basis of microreactor technology [7].

The photocatalytic process of oxidative decomposition of organics and hydrogen formation by reduction of protons, involves photo-excited states, i.e. electrons and holes (see for a schematic illustration Fig. 1) [8,9]. Photogenerated holes when reaching the semiconductor surface induce the formation of radical species, such as hydroxyl radicals, or organic radicals by reaction with surface

adsorbed organic compounds (Fig. 1). Usually conversion of the radical species and organic contaminants subsequently leads to formation of CO₂ and H₂O [4,8]. Several reports demonstrate that such decomposition of contaminants is feasible in anaerobic conditions, with simultaneous formation of hydrogen (Fig. 1) [10,11].

The catalyst most commonly used to induce the above illustrated reactions, is TiO₂ (and specifically P25) [12,13], with a bandgap of 3.2 eV and a conduction band (E_{CB}) energy lower than the standard redox potential of hydrogen ($E(H^+/H_2)$ 0V at pH 0), which makes hydrogen production thermodynamically feasible [14]. Unfortunately, hydrogen evolution is usually associated with low apparent quantum efficiency [8]. The reason is a high recombination rate between the photogenerated holes and electrons, before achieving the desired redox processes on the semiconductor surface [8]. This problem can be overcome by loading TiO₂ with noble metals, such as Pt, Pd, Au, Cu, or Rh [8,9,14,15]. These metals create effective surface sites for proton reduction, thus diminishing recombination of electrons and holes [14].

Decomposition of several organic compounds has been studied in anaerobic conditions, leading to production of hydrogen [16,17], such as alcohols [16,18], sugars [19], organic acids [16,20], and others [5,21]. Alcohols are the organic compounds that induced the

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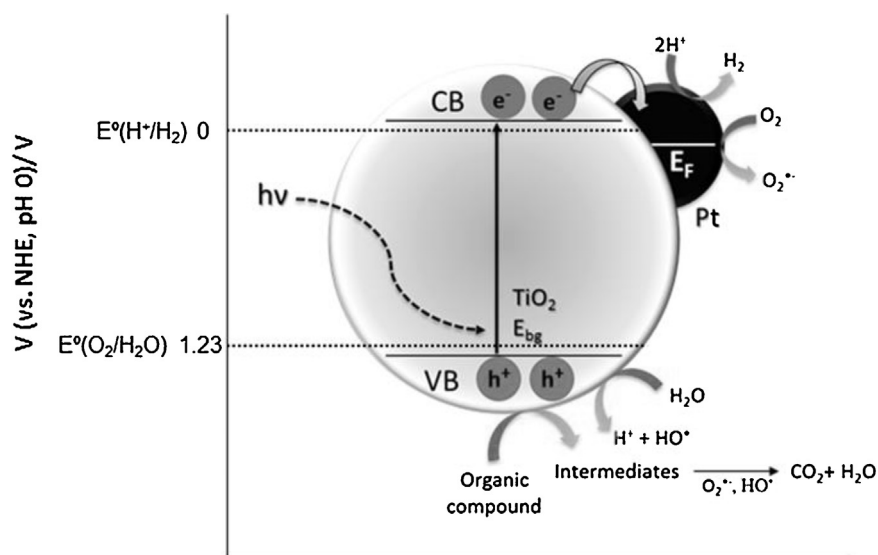


Fig. 1. Schematic illustration of TiO₂ loaded with Pt, and the processes occurring which are relevant for photocatalytic decomposition of organic compounds with simultaneous H₂ production.

highest rates in hydrogen evolution, likely due to their high susceptibility towards adsorption on oxidic surfaces and subsequent oxidation [22].

The aim of this paper is to demonstrate the effectivity of Platinized TiO₂ (P25) in the decomposition of methyl orange (MO), a dye that is often used as model compound in studies involving decontamination of wastewater, and the simultaneous production of hydrogen in the presence of excess MeOH. MeOH is known to induce hydrogen evolution very efficiently [9]. Both anaerobic, and oxygen lean conditions will be discussed, the latter condition representing water to be purified in domestic appliances.

2. Experimental

2.1. Materials

All reagents were obtained from Aldrich and used as received. Those include chloroplatinic acid, methanol and methyl orange. The photocatalyst material, P25 TiO₂, was obtained from Evonik Indus-

tries. The solvents (water and acetonitrile) used in the HPLC analysis were purchased from Biosolve.

2.2. Preparation of Pt-TiO₂

Deposition of Pt nanoparticles on TiO₂ P25 with an estimated weight loading of 0.5 wt-% was performed using a photodeposition procedure [23,24]. To this end, an aqueous suspension of TiO₂ P25 (0.5 g l⁻¹) and chloroplatinic acid (H₂PtCl₆, 0.5 g l⁻¹) was stirred for 30 min in the dark and then MeOH was added (1 M, 3 ml). The suspension was illuminated (radiation intensity 3.21 mW cm⁻² at 375 nm) for 5 h. The powder was collected by centrifugation, and washed three times consecutively with ethanol (20 ml), and finally with distilled water (20 ml). The powder was dried overnight at 90 °C.

2.3. Photocatalytic experiments

The equipment used for photocatalytic reactivity evaluation consists of three parts: a reactor, a gas chromatograph and a Lab-

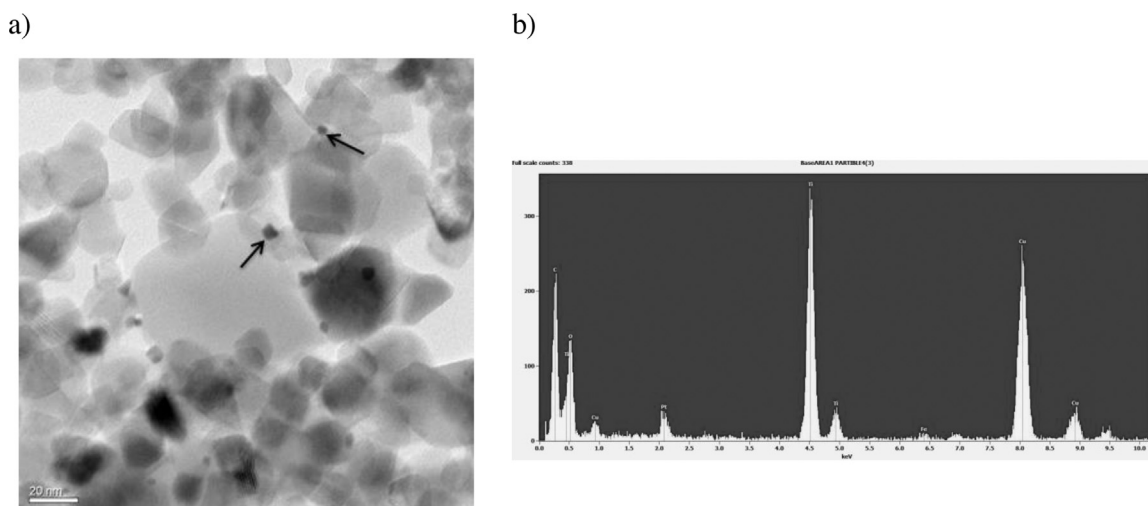


Fig. 2. Characterization of 0.5 wt-% Pt-P25. (a) TEM image with several Pt particles indicated by the arrows, and (b) an exemplary EDX spectrum of the particles, identifying the presence of Pt.

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