

Photoreforming of organics for hydrogen production: Microkinetic analysis and experimental validation

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Highlights

- A detailed reaction network was proposed to describe the photocatalytic production of hydrogen.
- Rate coefficients were estimated according to DFT and transition state theory.
- The resulting mathematical model was validated using experimental results.

1. Introduction

With a provided average daily energy of 10^{22} J – that would cover by far the global annual demand for energy – the sun represents the largest available renewable energy source. Thus, harvesting visible light and converting it into appropriate forms of energy has the potential to meet the current sustainability requirements by (i) covering the future energy demands and (ii) overcoming the serious environmental issues related to the use of fossil fuels [1]. Current commercial technologies (e.g. photovoltaic cells) can convert solar energy into electrical energy with a maximum efficiency exceeding 20% [2]. However, to make solar energy utilization viable, major improvements will be required to meet large scale energy storage. A viable complementary option is the conversion of solar energy into chemical energy via photoreforming of organics. This represents a renewable and eco-friendly technique to produce hydrogen and value-added chemicals via a waste abatement process [3]. An appropriate tuning of the selectivity of the process can result in the production of valuable compounds. In this work, we provided a microkinetic description of the photocatalytic hydrogen production process using transition metal loaded anatase as a model photocatalytic system.

2. Methods

Photocatalytic experiments were carried out in an annular glass batch reactor, equipped with high-pressure mercury vapour lamps, located in a quartz sleeve. The photocatalysts were prepared through in-situ photodeposition of transition metals (TM) on anatase nanopowder. To prevent the reaction between dissolved oxygen and photogenerated electrons, a nitrogen stream was bubbled into the solution 40 min before the photocatalytic runs. After that, selected concentrations of metal ions ($\text{TM}/\text{TiO}_2 = 10\%$ mol) were added to the mixture as salts. During the photocatalytic experiments, nitrogen was continuously bubbled into the reactor, at a flow rate of 0.30 L/min. After completion of the photodeposition process, gaseous samples were collected at fixed time differences to evaluate the hydrogen production rate. A daylight lamp was additionally used to assess the hydrogen production rate under visible light irradiations.

Periodic Density Functional Theory calculations were performed using Vienna Ab Initio Simulation Package VASP. Generalised Gradient Approximation GGA was employed using Perdew–Burke–Ernzerhof functional with Hubbard correction PBE + U. The U value was implemented for titanium Ti atoms alone and was selected to be $U = 4$ eV based on it being the most used in previous works performed on anatase-based systems [4]. The conventional (Ti_4O_8) anatase unit cell was modified to uncover the (101) surface and the cell relaxation of the $3 \times 2 \times 1$ supercell was performed. Slabs of anatase were created by introducing an 18 Å vacuum layer in between. TM atoms (Cu, Ag, Au, Pd, Pt) were placed in between the two 2-coordinated oxygen atoms (and on top of one 3-coordinated oxygen) on the anatase (101) surface to calculate the binding energy of the metal on the anatase surface.

Additionally, the hydrogen evolution reaction activity was evaluated by estimating the Gibbs free energy of hydrogen adsorption ΔG_H . The Charge Density Difference (CDD) distribution was plotted to investigate the charge increase (or decrease) on the hydrogen radical during the hydrogen molecule formation step.

3. Results and discussion

The experimental results obtained under UV light irradiation show the following order in catalyst activity in terms of hydrogen production rate Pt > Au > Pd > Cu > Ag > Bare anatase. Compared to the bare anatase case, all metal-loaded anatase cases show an electron density increase on the hydrogen radical, meaning faster hydrogen gas formation. The CDD analysis revealed that the TM@TiO₂ surfaces are considerable polarized with the electrostatic interactions playing a key role. This analysis revealed that loading anatase with platinum has the highest effect on the increase of electron density around the hydrogen radical while loading anatase with silver has the lowest effect. A reaction network was developed to describe the oxidation of the sacrificial agent and the simultaneous hydrogen production. When methanol was used as the model sacrificial agent, the first oxidation step of methanol to methoxy radical was recognized as the rate determining step upon identification of the transition state. Experimental runs conducted at various methanol concentrations showed a negligible increase in the hydrogen production rate at methanol concentrations higher than 1 mol/L indicating that methanol adsorption is described by a Langmuir-Hinshelwood model. The developed reaction network and the theoretically estimated rate coefficients were coupled with the design equations of a batch reactor to build a continuum kinetic model. The resulting system of differential equations was integrated using a numerical solver to simulate the experimental reaction kinetics and hydrogen production yields.

4. Conclusions

The combined computational/experimental microkinetic analysis presented in this work unravels mechanistic details of the photocatalytic hydrogen production and represents a powerful tool to predict the hydrogen evolution reaction kinetics obtained from experiments and design more efficient photocatalytic systems.

References

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Keywords

“Hydrogen production”; “Sacrificial photocatalysis”; “Microkinetic modelling”; “Reaction kinetics”.