

Photocatalytic hydrogen evolution activity of transition metal sulfides supported on TiO₂

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1. Scope

To address global warming, researches on the development of clean and renewable energy play a key role. Production of hydrogen by photocatalytic water splitting is one possibility.

Titanium dioxide (TiO₂) is highly studied for its photocatalytic properties on hydrogen evolution reaction (HER). However, alone its efficiency is not enough for catalytic applications. Since several years, efficient co-catalysts were designed to overcome the issue of electron-hole recombination and to improve the HER activity of the system. Noble metals are good co-catalysts; to this day, platinum supported on TiO₂ is the best one.

Regarding the cost of Pt-based catalyst, several alternatives were investigated. In particular, transition metal sulfides (TMS) seem to be good candidates. Molybdenum sulfide recently emerged as an alternative to noble metals for photocatalysis.^[1,2] The objective of this work is to screen several TMS for photocatalytic H₂ production and to understand reasons of their efficiency.

2. Results and discussion

Catalysts were prepared using a solution deposition method already reported by Girel et al.^[2] It is a preparation method easy to set up and with soft temperature and pressure conditions. Eight different TMS were deposited on CristalACTiV™ PC500 (TiO₂-anatase): cobalt, nickel, copper, molybdenum, ruthenium, silver, platinum and mercury sulfides.

HER performance was measured for each catalyst in a solution of isopropanol and water (50/50 %_{vol}). The following overall reaction is proposed: $\text{CH}_3\text{CHOHCH}_3 \rightarrow \text{CH}_3\text{COCH}_3 + \text{H}_2$

Isopropanol is oxidized by photogenerated holes and protons are reduced by photogenerated electrons. Instead of other alcohols, no side products are observed and the comparison of the different catalysts is easier. Hydrogen production rate (r_{H_2}) is measured at different temperatures (10, 20, 35 and 45°C) using a micro gas chromatography. An Arrhenius plot permits measurement of apparent activation energy (E_a). Quantum efficiency (QE) at 20°C and E_a were used to compare the activity of TMS supported on TiO₂ (Fig. 1). The latter is defined as the ratio between r_{H_2} and the flux photon received in the photoreactor (~1400 μmol/h). A 125 W high-pressure mercury lamp is used.

First, all of the eight TMS have a higher QE and a lower E_a than the PC500 alone, they all act as a co-catalyst of TiO₂. Secondly, RuS₂ is the best co-catalyst with a QE = 2.2% and E_a ~22 kJ/mol. Finally, for Mo and Pt based catalyst, a low E_a is determined but also a low QE. It shows that other parameters may be studied, as the number of active sites or photon absorption properties.

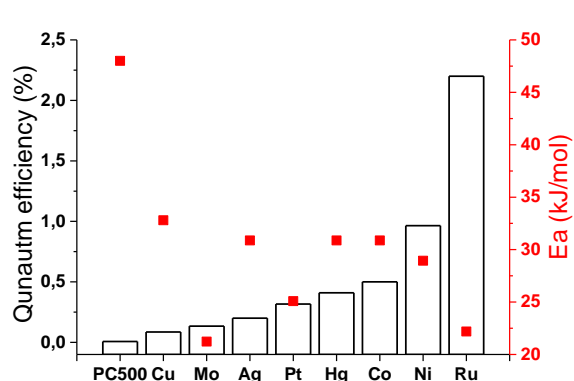


Figure 1

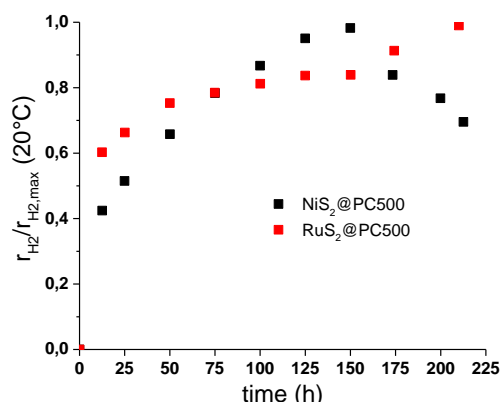


Figure 2

Figure 1: Quantum efficiency determined at 20°C (black bar chart) and activation energy (red square) of MS_x/PC500 photocatalyst with M=Cu, Mo, Ag, Pt, Hg, Co, Ni, Ru. Values for TiO₂ only are also given.

Figure 2: Ratio of the H₂ production rate with its maxima during a test of 220 hours for the co-catalyst NiS₂ (black square) and for the RuS₂ one (red square).

Based on the high efficiency of RuS₂ and NiS₂ co-catalyst, improvements were conducted changing the loading of TMS and the amount of sulfide. Stability of both catalysts was also studied (Fig. 2). Until 150 hours, temperature was fixed to 20°C. After that, successive cycles of 4 hours at 45°C and 20°C were conducted. Activation of RuS₂-based catalyst was observed whereas the NiS₂-based catalyst deactivated.

To explain better efficiency of RuS₂/PC500, valence band of Ag, Ni and Ru-based catalyst were investigated by X-ray photoelectron spectroscopy. In addition to the well-known TiO₂ signature^[3], another peak was observed and assigned to TMS contribution. For RuS₂ co-catalyst, relative contribution of the additional peak was fourth times higher than for NiS₂ and eight times higher than for Ag₂S. This observation will be discussed regarding the activity of each catalyst.

3. Conclusion

TMS emerged as good TiO₂ co-catalyst for HER photocatalysis. In comparison with Pt/TiO₂ their QE are still low but the cost is also roughly decreased. Methodology details above, consisting in measuring activation energy, may lead to a better understanding of photocatalytic mechanism and to the design of better catalysts. More characterization should be conducted on catalysts to understand their activation or their deactivation during a test. First evidence of a relationship between electronic structure of catalysts and their HER performance was observed. Deeper investigations must be done, UV-visible absorption will be used to determine the energy band gap, X-ray absorption spectroscopy and ultraviolet photoelectron spectroscopy will probe conduction and valence band, respectively.

References:

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