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On the photocatalytic and electrocatalytic hydrogen evolution performance of molybdenum sulfide supported on TiO_2

Etienne Girel, Eric Puzenat, Christophe Geantet, Pavel Afanasiev*

Institut de Recherches sur la Catalyse et l'Environnement de Lyon IRCELYON, UMR 5256, CNRS—Université Lyon 1, 2 av A. Einstein, 69626 Villeurbanne Cedex, France

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ABSTRACT

This study aimed to define key preparation and treatment parameters determining the hydrogen evolution reaction (HER) performance of molybdenum sulfide-based photocatalysts. Amorphous and nanocrystalline molybdenum sulfide catalysts supported on titania have been studied in photocatalytic and electrochemical HER. The results of HER measurements were compated to the thiophene hydrodesulfurization HDS activity. Titania polymorph plays a crucial role for HER: high-surface area anatase PC500 and anatase-rutile Degussa P25 show high HER performance, whereas rutile nanorods demonstrate poor activity. Two preparation methods applying impregnation and solution deposition techniques have been compared. Solution deposition affords superior activity, with a maximum HER rate for 0.5% wt. Mo loading, even if the dispersion of MoS_2 phase and HDS activity are better for impregnated systems. Therefore, for the photocatalytic performance not the dispersion of MoS_2 and abundance of edge sites but efficient electron hopping from the semiconductor to the co-catalyst is most important. In order to study the influence of the MoS_2 edges state, the solids reduced under H_2 or treated in pure H_2S were compared. The presence edge S_2^{2-} groups have a positive influence on the photo- and electrocatalytic HER activity.

1. Introduction

Direct conversion of solar energy to hydrogen from water via artificial photosynthesis is considered to be the most effective strategy to mitigate the global warming and to address the problem of alternative energy sources [1,2]. The production of H_2 by photocatalytic water splitting has attracted much attention as a clean and renewable solar H_2 generation system. Despite tremendous efforts on this direction, development of viable photocatalysts for water splitting remains among the greatest challenges in materials science. Titanium oxide TiO_2 is by far the most studied and the most efficient semiconductor for the photo catalysis applications [3]. Current research efforts are directed to the design of efficient co-catalysts, present on the surface of TiO_2 in order to facilitate the utilization of photogenerated electrons and holes.

Molybdenum sulfide recently emerged as an alternative to noble metals in electrocatalysis and photocatalysis [4]. However, unlike noble metals, MoS_2 is prone to modification of the structure due to oxidation and reduction processes, both possible in the aqueous medium. Many papers report on the application of MoS_x/TiO_2 for the photocatalytic decomposition of dyes [5–7]. While improved activity might result from addition of MoS_2 to titania, in the long term such catalysts are unstable, as MoS_2 is slowly but inevitably transformed to molybdenum oxides. Recently MoS_2 appeared to be a good catalyst for the hydrogen production, both electrocatalytic and photocatalytic [8]. Zong et al. have shown that MoS_2 on CdS nanoparticles are more efficient for the H_2 evolution than Pt on CdS [9,10]. However, CdS is a highly toxic pollutant. Other reports on the MoS_2 in combination with C_3N_4 [11–13]. Nevertheless, the performance figures still remain low as compared to the benchmark Pt on TiO_2 systems, even taking into account the differences between UV and visible energy fluxes in the solar spectrum.

While relatively recently emerged in the photocatalysis field, MoS_2/TiO_2 is a well-known heterogeneous catalyst for hydrotreating studied as such for many decades [14,15]. The properties of MoS_2/TiO_2 catalysts have been widely studied as a function of (doped) titania support properties and conditions of preparation/activation [16,17]. The preparation conditions influence the state of MoS_2 slabs edges as well as MoS_2 slabs stacking and length that in turn influence their catalytic performance. In this study we give insight into the influence of titania polymorph as well as preparation and activation treatment parameters on the photo(electro)catalytic performance of MoS_2/TiO_2 catalysts in HER.

* Corresponding author.
E-mail address: pavel.afanasiev@ircelyon.univ-lyon1.fr (P. Afanasiev).

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2. Experimental

2.1. Preparation of solids

Two series of solids were prepared, called "impregnated" and "deposited". Impregnated solids are prepared as conventional heterogeneous catalysts. Weighted amounts of titania were impregnated with aqueous solutions of ammonium heptamolybdate, dried in air at 120 °C overnight then calcined in air flow at 400 °C for 2 h. Sulfidation was carried out at 350 °C for 2 h in the gases mixtures 2%H_2S/H_2 or 10%H_2S/N_2 (vol.%).

"Deposited" MoS_x/TiO_2 solids were prepared by means of aqueous deposition of MoS_x species from aqueous solution and uses thioacetamide as a sulfur source and an acid to generate sulfide ions in solution. The preparation technique for "deposited" solids can be considered as a simplified version of earlier method reported by Liu et al., using hydrothermal conditions [18]. In a typical synthesis, 150 ml of aqueous suspension of 4 g TiO_2, 100 mg ammonium thiomolybdate and 1.5 g thioacetamide was refluxed under stirring for 1 h. Then 0.5 ml of 10 M HCl were added and the reaction mixture was refluxed for additional 30 min. The precipitate was separated and dried in air.

The molybdenum loading in the impregnated and deposited solids varied between 0.2 and 8 wt%. Even if we try to make obvious from the discussion, which catalyst is implied at any instance, self-explanatory catalysts designations are introduced. They begin with molybdenum loading in wt% followed by DMo for deposition and IMo for impregnation. Next follows the designation of the support (PC500, P25, Rutile) and finally (optionally) goes treatment condition. Thus 1DMoPC500-H350 designates 1 wt% Mo catalyst deposited onto PC500 titania and treated under H_2 flow at 350 °C.

Bulk molybdenum sulfide samples were prepared as references for the electrochemical study, using thiomolybdate decomposition, following the method used in [19]. The solid treated in H_2S is called MoS_2-S350, that heated under hydrogen flow is designated MoS_2-H350.

The reference catalyst containing 1 wt% Pt on Degussa P25 TiO_2 was prepared by impregnation, drying and reduction with H_2, as described in [20].

2.2. Characterizations

Temperature-programmed reduction (TPR) was carried out in a quartz reactor. The samples of sulfides (0.05–0.1 g) were heated under H_2 flow (50 ml min^{-1}) from room temperature to 1050 °C at a rate 5° min^{-1}. The H_2S produced in the reduction reaction was detected by a Thermo Prolab quadrupole mass-spectrometer. The amount of H_2S released from the solid was quantified after calibration of the MS detector with a gas mixture containing known H_2S content.

Transmission electron microscopy (TEM) was carried out on a JEOL 2010 device with an accelerating voltage 200 keV. The samples were dispersed in *n*-hexane by ultrasound, and then put onto a holey carbon on a copper grid. In order to protect them from oxidation by air, the samples still covered with liquid hexane were immediately introduced into the TEM vacuum chamber. The analysis of images (slabs stacking and length) was carried out using Digital Microgtaph Gatan™ software. Nitrogen adsorption isotherms were measured on a Micromeritics ASAP 2010 instrument. Specific surface area was determined using BET equation. Prior to measurements, the samples were heated in a secondary vacuum at 300 °C for 4 h. The X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance diffractometer with Cu-Kα emission and identified using standard JCPDS files. The metal content in the synthesized solids was determined, after dissolution in a HNO_3/H_2SO_4 mixture, by plasma-coupled atomic emission spectroscopy (ICP-ES Activa Jobin Yvon). Elemental analysis of light elements (CHNS) was performed on an analyzer Thermo Fisher Flash 2000. Raman spectra were recorded with a LabRam HR Raman spectrometer (Horiba-Jobin Yvon) equipped with a BXFM confocal microscope, interference and edge filters and a charge-coupled device detector. The exciting line of an Ar^+ ion laser at 514.5 nm or a He–Ne laser at 632.8 nm was focused using a ×50 long working distance objective.

2.3. Photocatalytic measurements

A batch slurry photoreactor was used in all experiments. A 125 W high-pressure mercury lamp with a quartz optical window was applied. The photon flux of this lamp integrated below 400 nm was 0.300 μmol/s. The photoreactor had two branches: the first to purge the system with argon before the reaction and the second one for sampling the gases during the reaction. The gases were analyzed with Agilent 3000A micro gas chromatograph. The volume of methanol or lactic acid solution used was 20 ml with a catalyst concentration of 1 g l^{-1}. The solution was magnetically stirred for 40–60 min, and the reactor was purged with Ar flow before the irradiation. Quantum yield (QY) has been calculated as HER rate (μmol/s) divided by photonic flux below 400 nm.

2.4. Thiophene HDS

Catalytic activities were measured for thiophene hydrodesulfurization (HDS) at atmospheric pressure in a fixed-bed flow microreactor. Reaction was carried out in the temperature range 280–340 °C, 50 ml/min gas flow, using 70–200 mg of catalyst and partial pressure of thiophene 2.7 kPa. The plug-flow reactor model was used to calculate the specific reaction rate, Vs, according to the equation

$$Vs = -(F/m)ln(1-x)$$

where F is the thiophene molar flow (mol/s), m is the catalyst mass (g), and x is the thiophene conversion. Catalytic activity was estimated at steady state conversion of thiophene, after ca. 16 h on-stream.

2.5. Electrochemical measurements

To prepare the electrodes, 5 mg of a solid was dispersed by ultrasound in a solvent containing 4 ml of ethanol and 1 ml of 0.5% Nafion solution, optionally containing 1 mg of acetylene black carbon. Then 10 μl of suspension was dropped onto rotating glassy carbon electrode (0.0706 cm^2), or on a 1 cm^2 FTO electrode (Aldrich, ~10 Ω/sq) and then dried in argon. The catalyst loading was about 0.6 mg/cm^2. The electrochemical measurements were performed on a Voltalab three-electrode potentiostat using a Pt counter electrode and Ag/AgCl reference electrode at 25 °C in purged by bubbling argon solutions of 0.1 M H_2SO_4, 0.1 M KOH or 0.1 M phosphate buffer (PB) at pH 1.0, 13.0 and 8.0 respectively. Cyclic voltammograms were obtained in the potential range from 0.5 to −0.1 V vs. Ag/AgCl at scan rates ranging from 20 to 200 mV s^{-1}. LSV scans were carried out at 2 mV/s rate.

3. Results and discussion

3.1. The influence of TiO_2 phase composition on the HER performance

TiO_2 exists in three phases as anatase, rutile and (less common) brookite. The anatase phase has been shown to be metastable with a band gap near 3.2 eV, while rutile is thermodynamically stable poly-

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