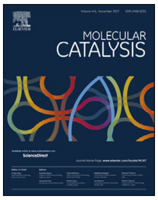
Molecular Catalysis 446 (2018) 88–97

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat



H_2 photo-production from methanol, ethanol and 2-propanol: Pt-(Nb)TiO_2 performance under UV and visible light

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ARTICLE INFO

Article history:
Received 13 November 2017
Received in revised form
15 December 2017
Accepted 16 December 2017

Keywords:
Anatase
Doping
Quantum efficiency and yield
Selectivity
Rate

ABSTRACT

In this work we analyzed the photo-production of hydrogen using titania-based systems able to profit from UV and visible light photons. For this purpose, we prepared Niobium-doped titania and a titania reference by a microemulsion method, subjected these oxide precursors to calcination and subsequently introduced Pt as co-catalyst by a chemical reduction method. These materials were characterized in terms of the structural and morphological properties of the oxide and metal phases. Using these materials, we measured the reaction rate and quantum efficiency of the hydrogen photo-production using methanol, ethanol, and 2-propanol as sacrificial agents. Significant activity enhancement was observed in the Niobium-doped material with respect to the titania reference material. The study focuses on interpreting the differences presented (between the two samples) among the three alcohols in the hydrogen yield and provides a physico-chemical study to understand the roots of the activity. Such study was mainly based on the analysis of the reaction mechanism using in-situ infrared spectroscopy together with the analysis of the energetics of the reaction taking into account the fate of the sacrificial alcohol during reaction.

1. Introduction

Hydrogen appears as an energy vector potentially important for a future where greener and more sustainable chemical processes are required. This is due to the fact that the molecule is ideal to store energy (ca. 3 times more than conventional natural gas per unit volume) and does not generate toxic or dangerous molecules during its chemical transformation to release energy [1]. Production of hydrogen trough photocatalysis using light and particularly sunlight and bio-derived molecules such as alcohols can provide a sustainable and attractive path with neutral carbon emissions, leading to a greener future [2–9].

Titania corresponds to the most utilized material in photocatalysis due to its inherent properties related to a modest cost, limited toxicity and outstanding chemical properties under illumination. However, its use is limited to the UV electromagnetic region due to its wide band gap, always above 3.0 eV. The use of sunlight requires, in a first approximation, the efficient handling of photons corresponding to the visible light region [1–8]. In the context of the photocatalytic production of hydrogen, the use of visible photons without compromising UV performance has been achieved by a number of methods. A successful one is the doping of the anatase material with specific cations such as B, Fe, Nb, Ce and others. Using Pt or noble metals as co-catalyst, the above mentioned doped titania samples displayed significant activity in the reforming of alcohols under UV and/or visible illumination [10–16].

Several bio-alcohols have been tested in the literature as sacrificial agents in the photo-production of hydrogen highlighting the importance of several experimental variables in order to maximize the production of hydrogen. Among them we can highlight the co-catalyst chemical nature and physico-chemical properties, charge carrier handling by the metal-support system, alcohol:water ratio, or the light wavelength and intensity [17–33]. Methanol is the simplest molecule from the structural and chemical points of view and probably the molecule receiving most attention due to the relatively high hydrogen production rates commonly observed [14,15,34–37]. Irrespective of the alcohol chemical nature, the studies show that hydrogen molecules are essentially produced stoichiometrically from the alcohol, although the hydrogen atoms are exchanged through scrambling with the corresponding atoms of water molecules of the media during the production process of

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https://doi.org/10.1016/j.mcat.2017.12.023
2468-8231/

the hydrogen molecule [36,38]. A schematic representation of the reactions that summarizes the most important chemical steps is as follows:

$$Cat + h\nu \rightarrow Cat + h^+ + e^- \quad (1)$$

$$h^+ + H_2O_{ads} \rightarrow OH^\circ + H^+ \quad (2)$$

$$RCH_2OH_{ads} + h^+ (OH^\circ) \rightarrow \text{Products} + \text{H}^+ (H_2O) \quad (3)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (4)$$

In brief, light absorption triggers the creation of electron and holes (Eq. (1)). These charge carriers reach the surface and produce several chemical species (Eqs. (2)–(4)). In the case of the alcohol reforming, holes or hole-related species such as hydroxyls are responsible of the attack (or oxidation) of the alcohol (Eq. (3)) while electrons are consumed in the production of hydrogen (Eq. (4)) [2–4]. A point usually dismissed in the literature is connected with the carbon-containing molecules produced in step 3. Hydrogen production depends critically on this issue or more specifically on the hydrogen remaining on the carbon-containing products due to the already mentioned stoichiometric relationship essentially holding between hydrogen production and hydrogen content of the sacrificial molecules [36,38].

Analysis of catalytic performance concerning the study of several alcohols as sacrificial agents has been presented for noble-metal promoted titania materials [25,39–41]. Alcohols having at least one hydrogen atom bonded to the (carbon) alpha position render higher reaction rates. Progress in understanding the differences in hydrogen production rates as a function of the alcohol nature showed the importance of alcohol polarity and the exponential of the alcohol potential oxidation in controlling the rate of hydrogen production [40,41]. However the understating of the physico-chemical interpretation of photo-activity in terms of alcohol chemical nature has not considered the chemical variable concerning the critical role that the different chemical products generated as a function of the alcohol chemical nature must have in hydrogen production. This point is obviously related to the chemical properties of the active centers transforming the alcohol sacrificial molecules.

In this contribution we study the hydrogen photo-production using several alcohols as sacrificial molecules and taking into account the use of UV and visible light illumination in order to progress in creating systems able to profit from sunlight. For this task we carried out a study using methanol, ethanol and 2-propanol and measured the reaction rates as well as the true quantum efficiency. Although all these molecules have hydrogen in alpha positions (to the hydroxyl moiety), significant differences in hydrogen photo-production rate are expected. We utilized titania and, more importantly, Niobium-doped titania as supports of the Pt-based catalysts in order to achieve high activity under both UV and visible illumination [14,15]. This work provides an interpretation of catalytic output concerning activity and selectivity of the alcohol photo-reforming reaction through an in-situ infrared analysis of the alcohol activation together with a thermodynamic analysis of the energy of the process and its connection with the hydrogen production rate.

2. Experimental

2.1. Preparation and characterization of catalysts

Materials were prepared using a microemulsion method by addition of Titanium tetraisopropoxide to an inverse emulsion containing either an aqueous solution of hydrated Niobium nitrate (Sigma) or just water dispersed in *n*-heptane, using Triton X-100 (Aldrich) as surfactant and hexanol as cosurfactant. Total cation content of the aqueous solution is 0.5 M. Water/(Ti+Nb) and water/surfactant molar ratios were, respectively, 111 and 18 for all samples. The resulting mixture was stirred for 24 h, centrifuged, decanted, rinsed with methanol and dried at 300 K for 6 h. Following the microemulsion preparation method, the amorphous powders were calcined under air for 2 h at 723 K. The co-catalyst was introduced subsequently by a chemical deposition method using a H_2PtCl_6 (Aldrich) solution. First, the calcined powder was suspended by stirring in a deionized water solution for 30 min. After that, the proper quantity of H_2PtCl_6 was added to the solution (to get a 0.5 wt.% of Pt on metal basis) and kept under stirring 5 min more. The reduction was carried out using a $NaBH_4$ (Aldrich) aqueous solution (Pt/$NaBH_4$ molar ratio 1/5). The final solid was rinsed with deionized water, collected by centrifugation and dried at 353 K. Samples are named Ti (Pt-TiO_2 reference system) and Nb (Pt-Nb doped-TiO_2). Niobium (when present) and Platinum content of the solids were measured with total reflection x-ray fluorescence (Bruker – S2 PicoFox TXRF Spectrometer) rendering values equal to 0.5 wt% for Pt in both catalysts and 2.5 mol% (cationic basis as $Nb_{0.025}Ti_{0.0975}O_x$) for the Nb sample within an error below 2.1and 1.5% for, respectively, Niobium and Platinum components.

XRD profiles of the samples were obtained using a polycrystal XíPert Pro PANalytical diffractometer using Ni-filtered Cu Kα radiation with a 0.02° step. Crystallite sizes reported were calculated from XRD patterns using the Williamson-Hall method which takes into account the strain and particle size contributions to the XRD peak broadening [42].The BET surface areas and average pore sizes and pore volumes were measured by nitrogen physisorption (Micromeritics ASAP 2010). UV–vis diffuse-reflectance spectroscopy experiments were performed on a Shimadzu UV2100 apparatus using $BaSO_4$ or Teflon as a reference, and the results presented as the Kubelka-Munk transform [43]. Band gap analysis for an indirect/direct semiconductor was done following standard procedures; e.g. plotting $(h\nu a)^n$ (n = ½ or 2 for indirect or direct semiconductor; hv = excitation energy, a = absorption coefficient, assumed to be proportional to the Kubelka-Munk transform in the relevant wavelength range) vs. energy and obtaining the corresponding intersection of the linear fit with the baseline [44].

Diffuse Reflectance Infrared Fourier Transform Spectra (DRIFTS) were taken in a Bruker Vertex 80 FTIR spectrometer using a MCT detector and running under OPUS/IR software. The set-up consists of a praying mantis DRIFTS accessory (Harrick Scientific) and a reaction cell (HVC, Harrick Scientific). The reaction mixture was prepared by injecting in a nitrogen carrier (50 mL min^{-1}) a 3:7 alcohol:water mixture (0.08 mL min^{-1}) with a syringe pump before entering the DRIFTS cell. The DRIFTS spectra were collected in the range of 4000–600 cm^{-1} with a resolution of 2 cm^{-1}, by averaging 10 scans over a total of 1.2 s. In DRIFTS experiments in-situ light excitation was carried out using 365 nm (488, 550 nm) radiation. A Hg-Xe 500 W lamp with a dicroic filter 280–400 nm coupled with a 365 nm (25 nm half-width) filter (LOT-Oriel) were used to select the light excitation. Each sample, without any previous treatment (expect flowing nitrogen for 10 min), was subjected in a continuous mode (without modifying gas mixture) to a single, multi-step experiment which aims to test the: *i)* adsorption of the reactive mixture under dark conditions, *ii)* reaction mixture evolution under illumination conditions, and *iii)* subsequent stay at dark conditions. Spectra were taken after different exposure times to verify any evolution behavior.

2.2. Description of reactor and catalytic outputs

Photocatalytic measurements at liquid medium were carried out using a cylindrical-type, batch pyrex (cutting absorption edge at ca. 300 nm) reactor of 4 cm depth (z coordinate in the numerical