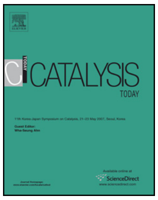
Catalysis Today xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

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



PtO_x-SnO_x-TiO_2 catalyst system for methanol photocatalytic reforming: Influence of cocatalysts on the hydrogen production

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ARTICLE INFO

Article history:
Received 21 September 2016
Received in revised form
19 December 2016
Accepted 7 February 2017
Available online xxx

Keywords:
Calcination
High temperature H_2 treatment
Cocatalyst
XPS
ESR
^1H MAS NMR

ABSTRACT

Effects of modification of PtO_x-TiO_2 photocatalysts by tin were elucidated by exploring relationships between the structural properties of variously prepared tin-loaded catalysts and their catalytic activity in methanol photocatalytic reforming. Tin free and amorphous tin-oxide decorated TiO_2 samples were prepared by sol-gel method from titanium-isopropoxide. In other approach, Sn was loaded onto the sol-gel prepared TiO_2 by impregnation followed by calcination. Pt was introduced by impregnation followed by either reduction in H_2 at 400 °C or calcination at 300 °C. TEM, XRD and Raman spectroscopic measurements proved that TiO_2 existed in the form of aggregates of polycrystalline anatase with primary particle size of 15–20 nm in all samples. Photocatalytic hydrogen production was influenced by the combined effect of many parameters. Both the presence of Sn and the way of Pt co-catalyst formation played important role in the activity of these photocatalysts. The Sn introduction by both sol-gel method and impregnation clearly enhanced the photocatalytic activity. ^1H MAS NMR measurements revealed that the Sn introduction reduced the amount of the terminal Ti-OH groups of relatively basic character considered to be unfavorable for the photocatalytic reaction. Presence of SnO_x decreased the signal of the undesirable vacancies observed by ESR. Furthermore surface SnO_x enhanced the dispersion of Pt. Formation of the Pt co-catalyst by calcination was more favorable than by H_2 treatment. In case of the calcined samples *in situ* reduction of the Pt nanoparticles at the beginning of the photocatalytic reaction was found to be favorable for the hydrogen production. The relatively modest photocatalytical activity obtained after high temperature H_2 treatment could be related to at least two processes in this system: (i) creation of unfavorable oxygen vacancies and (ii) segregation of SnO_x to the surface of the Pt cocatalyst as the result of the air exposure of the alloy type Pt-Sn nanoparticles formed during the H_2 treatment, resulting in a decreased number of active sites for reduction of H^+.

1. Introduction

Photocatalytic hydrogen production is a promising approach for transforming solar energy into chemical energy for storage [1]. Methanol which can be obtained from both fossil resources and biomass [2] is an appropriate starting compound for H_2 generation due to its high H/C ratio. Many efforts have been made for efficient photoinduced reforming of methanol on semiconducting oxides in the presence of water providing H_2 and CO_2 [3–6]:

$$CH_3OH + H_2O \overset{\text{Photocatalyst, } h\nu}{\rightleftharpoons} CO_2 + 3H_2 \quad (1)$$

Because of its efficiency, long term stability, cheapness and low toxicity, TiO_2 is one of the most frequently used photocatalysts [7–9]. Different types of sol-gel methods are widely applied for preparation of TiO_2 [10]. Benefits derived from preparing TiO_2 by sol–gel method include the synthesis of nanosized crystallized powder of high purity at relatively low temperature, resulting in homogeneity of the prepared materials. Sol-gel methods give possibility to introduce doping elements [11–14] or their combination simultaneously [15], to prepare composite type TiO_2-based materials [16,17]. The sol-gel method is a possible way to obtain coatings or nanocoatings [18], porous films [19] or ordered mesoporous structures [20,21].

The activity of TiO_2 in reaction (1) can be increased at least an order of magnitude when a proper cocatalyst is involved [3,22,23]. The advantages of the cocatalysts are attributed to the reduced

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http://dx.doi.org/10.1016/j.cattod.2017.02.009
0920-5861/

Please cite this article in press as: E. Tálas, et al., PtO_x-SnO_x-TiO_2 catalyst system for methanol photocatalytic reforming: Influence of cocatalysts on the hydrogen production, Catal. Today (2017), http://dx.doi.org/10.1016/j.cattod.2017.02.009

charge recombination; promoted charge separation and transport driven by junctions/interfaces [24,25]. Another important role of the cocatalyst is to provide reaction sites for elementary reaction steps subsequent to light absorption, such as formation of molecular hydrogen and its desorption from the surface [24,25]. If the surface reaction is too slow to consume the charges, the probability of charge recombination increases. Pt is a very effective cocatalyst for H_2 production [3,25] as it shows the lowest activation energy for H_2 evolution [25,26].

In order to load metal nanoparticles on the surface of the semiconductors several different methods are available. Commonly used techniques include *in situ* photodeposition [27,28] and deposition of pre-prepared metal colloids [29,30]. The traditional way for preparing supported metal nanoparticles is impregnation with the appropriate metal salt followed by high temperature hydrogenation [31]. Calcination of the metal salt loaded on semiconductors by impregnation also resulted in effective cocatalysts for photocatalytic H_2 production [32].

In our previous work sol-gel synthesis carried out in the presence of tin compounds under relative mild conditions (*i.e.* temperature of calcination: 400 °C) was used for preparation of TiO_2 based photocatalysts [33]. Our TEM and SEM measurements indicated the presence of micron sized aggregates built from polycrystalline anatase in those samples. XRD and Raman spectroscopic measurements proved the formation of pure anatase by our method. No evidence for tin incorporation into the lattice of TiO_2 was found by the above characterization methods. Nevertheless band broadening in Raman spectra and surface enrichment in Sn detected by XPS suggested that TiO_2 decorated with amorphous tin-oxide islands was obtained [33]. This type of tin-oxide together with metallic Pt nanoparticles formed by high temperature hydrogen treatment as a cocatalyst system considerably improved the photocatalytic activity of TiO_2 in the methanol photocatalytic reforming reaction [33]. Although supported Sn-Pt bimetallic catalyst are widely studied and used in various fields, there are relatively few reports dedicated to the characterization of the cocatalysts in the PtO_x-SnO_x-TiO_2 photocatalytic system up to now [34–36]. To the best of our knowledge no systematic study of the effect of cocatalyst formation in these systems exists; only influence of redox-treatment on Pt/TiO_2 system has been described [37]. Reviewing the literature on Pt/TiO_2 systems with Pt cocatalyst loaded by different way, certain indication can be found that the ionic state of the Pt is favorable for the photocatalytic reaction [38–40].

In this work a detailed study of the influence of the way of cocatalyst formation (hydrogen treatment *vs.* calcination after the impregnation of the Sn-containing sol-gel TiO_2 with platinum salt) is given. The focus is laid on the state of platinum and tin in the cocatalyst as well as the cocatalyst-TiO_2 interaction. We try to find relationships between the catalytic activity observed in methanol photocatalytic reforming and the structural properties of the platinum- and tin-loaded sol-gel TiO_2. In order to obtain more realistic picture about the real working catalyst, results of characterization of fresh and recovered samples are compared.

2. Material and methods

2.1. Materials

Titanium-isopropoxide (≥97.0% % Sigma Aldrich) was used for the synthesis of titania nanoparticles. $SnCl_4{\cdot}5H_2O$ (Riedel-de Haen) was used as tin precursor. Citric acid (Sigma Aldrich) was used for gel formation. $Pt(NH_3)_4(NO_3)_2$ (Aldrich) was used as a precursor of supported Pt nano-particles. Methanol, absolute ethanol solvent and hydrochloric acid (37 w%) and nitric acid (65 w%) were products of Reanal.

2.2. Synthesis of photocatalysts

Tin free (no-Sn) and tin modified (SnOx-SG) TiO_2 samples were prepared by a sol-gel method as described before [33]. Briefly, in the presence of citric acid and absolute ethanol titanium-isopropoxide was stirred for 180 min at room temperature and then heated at 65 °C until gel formation. In case of tin modified samples $SnCl_4{\cdot}5H_2O$ was also introduced into the mixture at Sn/Ti ratio of 0.007. The gel was dried, thereafter calcined for 5 h at 400 °C; the choice of the calcination temperature was restricted to relatively low values as we wanted to ensure the formation of the pure anatase phase in order to make easier the interpretation of the catalytic behavior of our system. In another approach, Sn was loaded onto the sol-gel prepared TiO_2 by incipient wetness impregnation with $SnCl_4{\cdot}5H_2O$ solution followed by calcination at 300 °C (SnOx-I). The Sn load was 1 w% in both cases. Pt was introduced from aqueous solution of $Pt(NH_3)_4(NO_3)_2$ by incipient wetness impregnation. Contrary to our previous work [33] the Pt load was increased to 1% which allowed the photoelectron spectroscopic (XPS) analysis of the supported platinum. The dried samples were either reduced for 1 h at 400 °C in H_2 atmosphere or calcined for 1 h at 300 °C. The sequence of the introduction of Sn and Pt was also varied. The lineage of the various Sn-Pt/TiO_2 catalysts is depicted in Fig. 1.

2.3. Characterization of photocatalysts

Nitrogen adsorption isotherms have been measured in volumetric equipment (ASDI RXM 100, Advanced Scientific Design Inc.) in order to determine BET specific surfaces. Samples were pretreated in inert gas flow at 200 °C for 1.5 h then evacuated and cooled to the temperature of liquid nitrogen.

Raman spectra were recorded with a dynamically aligned Bio-Rad (Digilab) dedicated FT-Raman spectrometer equipped with a Spectra-Physics Nd-YAG-laser (1064 nm) and high sensitivity liquid-N_2 cooled Ge detector. The laser power used was about 250 mW at the samples. The resolution of the Raman instrument was ca. 4 cm^{-1} and a backscattered geometry was used. For each spectrum 256 individual spectra were averaged.

Diffuse reflectance UV–vis spectra of the samples were registered using a Jasco V-570 UV–vis spectrophotometer equipped with a NV-470 type integrating sphere. The data were collected between 800 and 200 nm wavelengths with 100 nm/min speed.

The solid state magic angle spinning (MAS) ^1H spectra of the samples were recorded on a Varian NMR System (Varian Inc., Palo Alto, CA, U.S.A.) operating at ^1H frequency of 400 MHz with a Chemagnetics T3 4.0 mm narrow bore double resonance probe. The ^1H direct polarization spectra were measured with a rotor spinning rate of 12 kHz.The ^1H $\pi/2$ pulse was 3 μs and a repetition delay of 5 s was used. The measuring temperature was 20 °C. Spectra were recorded before and after evacuation of the samples in a vacuum oven at 130 °C for 6 h.

The ESR experiments were performed with a Bruker Elexsys E500 X-band spectrometer. A typical microwave power of 1 mW and 1 G magnetic field modulation at ambient temperature were used. The magnetic field was calibrated with an NMR field meter. Signal intensity, linewidth and g-factor (spectroscopic splitting factor) values were used to characterize the samples. The knowledge of the g-factor can give information about a paramagnetic center's electronic structure.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using an EA125 electron spectrometer manufactured by OMICRON Nanotechnology GmbH (Germany). The photoelectrons were excited by both MgKα (1253.6 eV) and AlKα (1486.6 eV)

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