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Synergism and photocatalytic water splitting to hydrogen over M/TiO_2 catalysts: Effect of initial particle size of TiO_2

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ABSTRACT

In order to study the effect of anatase/rutile phases of TiO_2 on the photo-catalytic production of hydrogen (often invoked as synergism) two series of Pt/TiO_2 materials were prepared. The initial phase of TiO_2 in both series is anatase but their particle size is different. In one case the mean particle size of TiO_2 is ca. 15–20 nm (nano) and in the other it is ca. 100 nm (micro). Before the deposition of Pt, the two semiconductors (nano and micro) were heated to elevated temperatures to obtain partial (and total) transformation of the anatase phase to the rutile phase (UV–vis, XRD, XPS-valence band). On this differently prepared mixed phases Pt was deposited (ca. 1 at.%; corrected XPS Pt4f/Ti2p = ca. 0.05) and each series was tested for the photocatalytic production of hydrogen from water in presence of ethanol (5 vol.%) as a sacrificial agent (under identical conditions). Based on rates per unit mass no synergism for hydrogen production was seen in both cases; this is in part due to the decrease in the BET surface area during the phase transformation. However, strong synergism was observed for hydrogen production rates per unit area when the initial starting semiconductor was anatase nano (while no synergism seen in the case of the micro crystals). Maximum rate observed was in the 10–30% rutile range. Possible reasons for these differences are discussed.

1. Introduction

Hydrogen production from water can be obtained via many methods including solar thermal water splitting [1], combined photovoltaic and electrolysis [2], photo electrochemical processes [3] and photo catalysis [4]. Photocatalytic hydrogen production reactions carried out on semiconductor materials relies on many factors including band gap energies, band edges (conduction and valence band energy positions), electrons and holes diffusion, electron–hole recombination rates [4], bulk structure [5], surface structure [6,7] and defects [8–10].

TiO_2, among the most active photocatalytic semiconductor material, consists of several polymorphs the most common of them are anatase with a band gap of 3.2 eV and rutile with a band gap of 3.0 eV at room temperature. The lifetime of electrons in anatase and rutile phases using time resolved microwave conductivity measurements (TRMC) was studied on powder [11] and single crystals [12] and in both cases charge carriers in anatase were found to have longer life time than those in rutile. For hydrogen production from water and organic compounds the anatase phase is more active than the rutile one [13,14]. To increase the electron life time metal deposition on the semiconductor surfaces such as Ag, Rh, Au, Pt and Pd, are routinely used while to increase the hole life-time organic compounds such as alcohols and glycols are added into the aqueous media.

Mixed phase TiO_2 anatase and rutile have however shown, in many reports, superior activity than the expected arithmetic sum of that of anatase and rutile separately. This observation that falls under synergism has been the subject of considerable studies [15]. For example the rate of hydrogen production from ethanol over 1.5 wt.% Au/P25 (85% anatase and 15% rutile) is about two times higher than that seen over 2 wt.% Au/anatase alone and the latter is about 100 times more active than that of 2 wt.% Au/rutile; no matter is the expression of the rate (per unit area, unit mass or normalized to the XPS Au4f/Ti2p signal) [16]. Similar observations were reported over Pt/TiO_2 anatase, rutile and their mixtures [17]. Others [18] studied the photocatalytic activity of anatase and rutile phase in the visible region. The activity of the mix phase under visible light was explained as due to the lower band gap (3.0 eV) rutile polymorph where the photoexcitation mainly occurred in rutile phase with electrons being transferred to anatase phase. Nair et al. [19] proposed the interfacial model for the synergistic effect between anatase and rutile under UV and visible light. The transfer of electrons from rutile to anatase in the presence of visible light and

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migration of electrons from anatase to rutile in case of UV light was reported; the formation of potential charge barrier at the interface contributed in the proposed mechanism.

In this study, the effect of anatase to rutile ratios on the photocatalytic activity coupled with crystallite (particle) size on the phase transformation of anatase to rutile were investigated. Two different grades of TiO_2 one with large crystallite size (micro) and the other with small crystallite size (nano) were used. TiO_2 samples were annealed at different temperatures to get the varying percentages of anatase and rutile. Transformation of anatase to rutile depends on many factors including impurity content [20,21], temperature [22,23], pressure [24] and particle size [25,26]. The effect of initial particle size and the annealing temperature were studied here. The annealed TiO_2 samples containing different ratio of anatase and rutile were then impregnated with Pt and evaluated for the photocatalytic H_2 production from water using ethanol as a sacrificial agent. We have opted to use Pt because it is well studied on TiO_2, well dispersed, easily reduced and has among the lowest over-potential [27]. We find no synergism when the initial phase was micro size anatase particles but considerable synergism (on the rate once normalized to unit area) when the initial TiO_2 anatase particles where of nano-size.

2. Experimental

Two different series of 1 wt.% Pt/TiO_2 were prepared by wet impregnation. TiO_2 powder sample containing pure anatase phase obtained from Sigma Aldrich of about 20 nm size labeled as TiO_2 (nano) and the one obtained from Fisher Scientific of about 0.1 μm labeled as TiO_2 (micro) were used as the starting materials. TiO_2 (nano) powder was annealed isochronally (for 1 h) at different temperatures in the 700–800 °C range while TiO_2 (micro) powder was annealed isothermally at 1000 °C for different intervals of time. These conditions were found to be the optimum ones to obtain the mixed phase from each sample. Metal precursor solution was prepared by dissolving calculated amount of metal salt ($PtCl_2$ obtained from Sigma Aldrich) in 1 N HCl. The calculated amount of precursor solution was then impregnated to each of the annealed samples prepared. The impregnated mixture was subjected to stirring and was left at 70–80 °C overnight. The resulting slurry was then dried at 100 °C for 24 h, followed by calcination at 350 °C for 5 h in air. Following the above mentioned procedure, two series of 1 wt.% Pt/TiO_2 (nano and micro) were obtained.

The powder XRD patterns of the samples were recorded on a Philips X'pert-MPD X-ray powder diffractometer. A 2θ interval between 10 and 90θ was used with a step size of 0.010θ and a step time of 0.5 s. The X-ray, Ni-filtered Cu $K\alpha$ radiation source ($K\alpha = 1.5418$ Å), operated at 45 mA and 40 kV. The percentages of rutile in the mixed phase were calculated by the expression below [28] and are presented in Table 1.

$$\%\text{Rutile} = \frac{1}{\left[(A/R) \times 0.884 + 1\right]} \times 100$$

X-ray photoelectron spectroscopy was conducted using a Thermo scientific ESCALAB 250 Xi, The base pressure of the chamber was typically in the low 10^{-10} to high 10^{-11} mbar range. Charge neutralization was used for all samples. Spectra were calibrated with respect to C1s at 285.0 eV. Pt4f, O1s, Ti2p, C1s and valence band energy regions were scanned for all materials. Typical acquisition conditions were as follows: pass energy = 30 eV and scan rate = 0.1 eV per 200 ms. Ar ion bombardment was performed with an EX06 ion gun at 1 kV beam energy and 10 mA emission current; sample current was typically 0.9–1.0 nA. Self-supported oxide disks of approximately 0.5 cm diameter were loaded into the chamber for analysis. UV–vis absorbance spectra of the powdered catalysts were collected over the wavelength range of 250–900 nm on a Thermo Fisher Scientific UV–vis spectrophotometer equipped with praying mantis diffuse reflectance accessory. Absorbance (*A*) and reflectance (%*R*) of the samples were measured. The reflectance (%*R*) data was used to calculate the band gap of the samples using the Tauc plot (Kubelka–Munk function). BET surface areas of catalysts were measured using Quantachrome Autosorb analyzer by N_2 adsorption. Catalysts were evaluated for hydrogen production in a 100 mL volume Pyrex glass reactor. 25 mg of catalyst sample was introduced into the reactor. The catalyst sample was then reduced under hydrogen flow at 350 °C for 1 h followed by purging with nitrogen gas for 30 min. Milli-Q deionized water (20 mL) and the sacrificial agent (1 mL i.e. 5% by volume) of ethanol were added into the reactor. The final mixture was subjected to constant stirring initially under dark condition for some time to get better dispersion of catalyst powder and the sacrificial agent in the water mixture. The reactor was then exposed to the UV light; a 100 Watt ultraviolet lamp (H-144GC-100, Sylvania par 38) with a flux of ca. 2 mW/cm^2 at a distance of 10 cm with the cut off filter (360 nm and above). Product analysis was performed by gas chromatograph (GC) equipped with thermal conductivity detector (TCD) connected to Porapak Q packed column (2 m) at 45 °C and N_2 was used as a carrier gas.

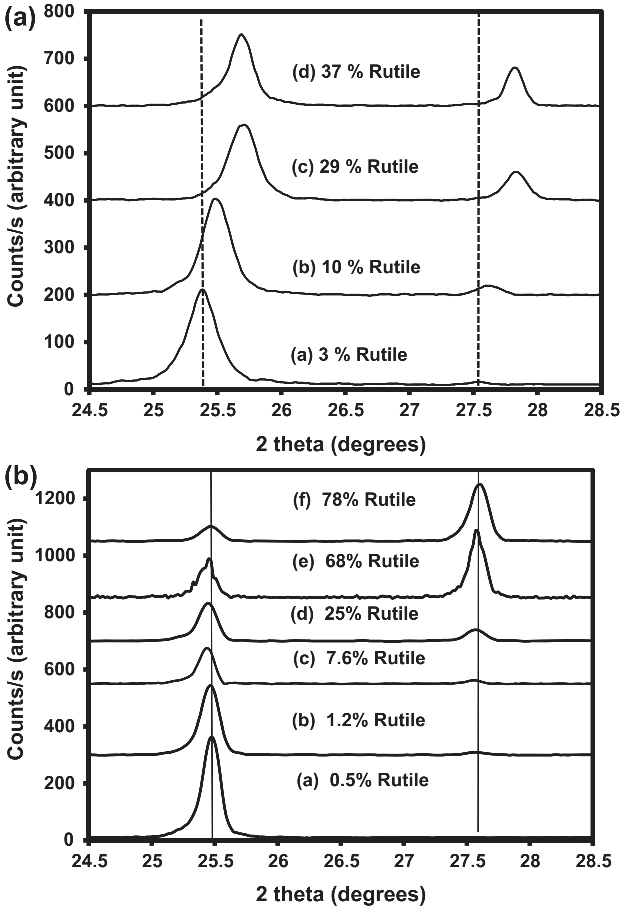

Fig. 1. (a) XRD pattern of TiO_2 (nano—initially anatase) annealed for 1 h in the 700–800 °C range. (b) XRD pattern of TiO_2 (micro—initially anatase) annealed at 1000 °C for different periods of times (in hours) to obtain the indicated rutile %.

3. Results and discussion

XRD was carried out to study the phase transformation of anatase to rutile of TiO_2 (nano and micro) powders. Fig. 1a and b shows the gradual transformation of the anatase phase into rutile