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Enhanced photocatalytic activity of octahedral anatase particles prepared by hydrothermal reaction

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ABSTRACT

Octahedral anatase particles (OAPs) were prepared by hydrothermal reaction (HT) with various experimental conditions, including different amounts of titanate nanowires (TNWs), different water volumes and different pH values, to obtain products with high contents of OAPs. The properties of photocatalysts were investigated by XRD, SEM, TEM, XPS and time-resolved microwave conductivity (TRMC). Photocatalytic activities for oxidative decomposition of acetic acid (CO_2 system) and anaerobic dehydrogenation of methanol (H_2 system) were tested. It was found that a larger amount and concentration of TNWs, as well as higher pressure during HT, resulted in the formation of smaller crystallites with higher density of mobile electrons. Enhanced photocatalytic activity, achieved for samples with the best morphology (higher content of OAPs), correlated with slower TRMC signal decay, i.e., slower recombination of charge carriers (e^-/h^+) probably due to lower content of deep electron traps. It was found that properties of platinum nanoparticles, deposited in-situ in the H_2 system in the absence or presence of pre-sparged oxygen, and their connection with OAPs were decisive factors for photocatalytic activity.

1. Introduction

Titanium(IV) oxide (titania, TiO_2) has been widely applied for environmental purification because of its many advantages such as good stability, strong redox ability, nontoxicity, cheapness and high availability [1,2]. The influence of titania structural/physical properties on the photocatalytic activity has been extensively studied. Results of previous studies suggested that higher crystallinity, larger specific surface area, smaller crystalline size and specific morphology (exposed crystal facets) resulted in higher photocatalytic activity [3,4].

Although particle morphology has been suggested to be an important factor for the activity of the photocatalyst [3,5–8], no direct proof was presented for that until our recent study in which the morphology of octahedral anatase particles (OAPs) was shown to be a key factor for the photocatalytic activity [9]. Direct evidence for OAP samples possessing almost the same properties (crystallinity, crystalline size, specific surface area and total amount of electron traps) and differing only by morphology has been presented, i.e., direct correlation between morphology and photocatalytic activity. It has been proposed that facetted anatase of an octahedral shape is responsible for the preferential distribution of shallow electron traps (ETs) rather than deep ETs, enabling greater mobility of electrons instead of their permanent trapping.

Titania with different morphologies has been prepared by various methods including hydrothermal reaction (HT), solvothermal, sol-gel, electrosynthesis and gas-phase methods [8,10–12]. HT is one of the most popular methods for titania synthesis due to feasible preparation of required nanostructures by simply changing the process conditions [3]. It is possible to modulate all HT conditions including HT temperature [6], HT duration [3,6], precursor amount, additives content [13], solvent volume [14], pH value of the reaction suspension [3], and pre- and post-treatment operations such as ultrasonication, calcination and grinding. For example, it was reported that crystal phase, shape and size of titania particles depended significantly on pH value of the peroxo titanic acid solution and HT duration [3].

Our previous study showed the effects of HT temperature, HT duration, ultrasonication duration, calcination and grinding on preparation of OAPs [15,16]. It was found that morphology governed photocatalytic activity, i.e., the higher the OAP content was in the final product, the higher was the photocatalytic activity. It is thought that changes in the content of reagents and pressure during the HT process (suspension/air ratio) influence the morphology of the final product and thus its photocatalytic activity. Therefore,

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in the present study, contents of the precursor and water as well as pH value of the reaction suspension were investigated.

2. Materials and methods

Potassium titanate nanowires (TNWs), prepared by HT of Evonik P25 titania (Nippon Aerosil) and potassium hydroxide solution [17], were used as the precursor for fabrication of titania samples containing OAPs. TNWs (100–1067 mg) were ultrasonically dispersed in Milli-Q water (30–40 mL) for 1 h, and then the suspension was put into a 100-mL sealed Teflon bottle into which an additional portion of Milli-Q water (20 or 40 mL) was added when necessary. The bottle was placed into an outer sleeve of a stainless autoclave and then heated in an oven for 6 h at 433 K. The obtained suspension was dispersed by ultrasonication for 10 min and then centrifugally separated (12000 rpm, 20 min). The white precipitates were collected and dried overnight under vacuum (353 K, 12 h). HT processes were performed for seven weights of TNWs (100, 133, 200, 267, 400, 533 and 1067 mg) and three volumes of water (30, 60 and 80 mL). The codes of the samples were defined as follows: TNW amount/water volume. For example, a 267/80 sample was prepared with 267 mg of TNWs and 80 mL of water.

The morphology was characterized by electron microscopy (SEM, TEM and STEM). Crystalline size and aspect ratio were estimated by XRD analysis. Experimental details are presented in SI.

The oxidation states of elements and surface compositions of samples were determined by X-ray photoelectron spectroscopy (XPS), and charge-carrier dynamics was determined by the time-resolved microwave conductivity (TRMC) method (details in SI).

Photocatalytic activities for (a) oxidative decomposition of acetic acid and (b) anaerobic dehydrogenation of methanol were examined. In each experiment, 50 mg of the photocatalyst was suspended in 5 mL of aqueous solution containing (a) 5.0-vol% acetic acid and (b) 50-vol% methanol and then photoirradiated under (a) air and (b) argon with magnetic stirring. Photoirradiation (>290 nm) was performed using a 400-W high-pressure mercury lamp under thermostatic control at 298 K. In the case of reaction (b), hexachloroplatinic acid was added before photoirradiation to be reduced in situ by photoexcited electrons to zero-charged platinum metallic deposits. Amounts of liberated CO_2 (a) and H_2 (b) in gas phase were determinated by gas chromatography (TCD-GC). The photocatalytic activities are presented as relative values to those of the commercial anatase titania photocatalyst FP-6 (Showa Denko Ceramics) that was simultaneously tested (details in SI).

To prepare smaller platinum NPs, Pt was also deposited for oxygen-saturated suspension (15-min pre-bubbling), in which photogenerated electrons were firstly consumed by oxygen hindering formation of platinum NPs (Fig. S2).

3. Results and discussion

3.1. Influence of the content of reagents

3.1.1. Photocatalyst characterization

The yield of the HT process was 60–76% with only the exception of the sample prepared with the smallest content of reagents (100/30), for which 48% yield was obtained. XRD patterns of HT products are presented in Fig. 1. Preparation conditions of HT were the same for all samples, i.e., 1-h ultrasonication, 433-K HT, 6-h HT, under which samples with the best morphology (highest content of OAPs) and thus highest photocatalytic activity could be obtained [9]. It was confirmed by XRD analysis that these conditions are sufficient for efficient conversion of TNWs into anatase. Crystallographic characteristics of all samples were almost the same, i.e., the same position and intensity of XRD peaks, indicating that the content of reagents did not influence crystallinity. Magnification of a representative XRD pattern (Fig. 1, center) showed that only one crystalline phase was formed during the HT process, i.e., anatase, being in agreement with the results of our previous study showing that samples prepared under the same HT conditions possessed almost the same crystallinity, while shortening of the HT and lowering of its temperature resulted in incomplete reaction and thus in the presence of TNWs in the final products [9]. Similarly, pre- and post- treatment operations such as ultrasonication, calcination (even up to 1173 K) and grinding did not influence the crystallinity of OAP-containing samples [16]. Therefore, it is concluded that only temperature and duration of the HT process are decisive for crystallinity of OAP-containing samples, while the effects of concentration and pressure during the HT process as well as pre- and post-treatment operations on anatase formation are negligible. The HRTEM image of the 267/80 sample confirmed the presence of single crystalline anatase (Fig. 1, right) due to a 0.35-nm lattice distance between fringes and the angle of 68.3° between (001) and (101) facets corresponding to anatase crystals, as has already been reported [7]. Crystalline sizes changed only in a narrow range from 15.8 to 17.8 nm, confirming the independence of crystalline properties on content of reagents.

Although, there was little variation in crystalline size, there was a clear correlation between the size and reagent content, especially for amount of TNWs, as shown in Fig. 2 (left). It was found that crystalline size decreased with increase in both the amount and concentration of TNWs (Fig. S3). However, a reverse correlation was found for aspect ratio (AR) change, i.e., increase of AR with increase in concentration of TNWs, suggesting that larger crystallites possessed smaller AR, as shown in Fig. 2 (right). These findings indicate that a higher concentration of TNWs results in either a steric effect and/or squeezing force, causing formation of elongated and smaller NPs. Obviously, this also results in simultaneous deformation of the perfect octahedral shape possessing an aspect ratio of 1.59. It is thought that additional four (100) facets can be formed between two (101) pyramids (nanoparticles encircled in Fig. 3), as was proposed for anatase nanorods prepared with hydrogen titanate in the presence of NaCl [14]. Summarized data are shown in Table S1.

The results of our previous study showed that changes in the conditions of HT (HT temperature, HT duration and US duration) resulted in a change in AR only in a narrow range of 1.6–1.8 [15]. On the other hand, post-treatment operations resulted in simultaneous changes in both crystalline size and AR in broad ranges of 17–110 nm and 0.7–1.7, respectively, i.e., temperature increase caused sintering and fusion of crystallites. For example, calcination at 1173 K resulted in formation of crystallites of 110 nm possessing AR of only 0.72. Present data indicate diminishing and narrowing of crystallites, resulting in the highest AR of ca. 1.9 for samples prepared with higher concentration of TNWs (6.66 g mL^{-1}) and larger volumes of water (60 and 80 mL). It is known that one of the most important parameters during the HT process is water volume, which directly correlates with remaining free space and thus with resultant pressure during the reaction. Moreover, change in solvent volume or precursor amount results in change in concentration. It should be pointed out that the 133/80 sample possessing an almost ideal AR of 1.61 was prepared with the largest volume but with the smallest amount and concentration of TNWs. Therefore, it is concluded that concentration of TNWs rather than pressure inside the reactor is decisive for formation of perfect anatase crystals.

The morphology of samples was investigated by SEM observation, and exemplary SEM images with respective values of total OAP content are shown in Fig. 3. It is clear that different morphologies were obtained for OAP products prepared under different synthesis conditions. The 267/80 and 533/80 samples had the highest and the lowest contents of OAPs, respectively. In general, an increase in the concentration of TNWs resulted in a decrease in OAP con-

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