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Detailed XPS analysis and anomalous variation of chemical state for Mn- and V-doped TiO_2 coated on magnetic particles

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ABSTRACT

Manganese (Mn)- and vanadium (V)-doped titania (TiO_2) coated on iron oxide (γ-Fe_2O_3) nanoparticles (TM and TV) were reduced in H_2/N_2 mixture atmospheres at different reducing temperatures T_R. Furthermore, TM and TV reduced at T_R = 800 °C (TM8 and TV8) were subsequently nitrided in the ammonia (NH_3) atmosphere at different temperatures T_N in order to change the chemical state (CS) of the Mn, V, Fe, Ti, O, and N elements. Samples were characterized by X-ray diffraction and X-ray photoelectron spectroscopy. For reduced samples, with increasing T_R, anomalous variation of CS is as follows: Ratios of V^{4+} and V^{5+} increased, while the ratio of V^{3+} decreased, and the ratio of oxygen vacancy O_v decreased. Data conflict with the effect of reduction reaction could be understood as follows: O_v was occupied by O from H_2O (product of the reduction reaction), according to previous theoretical result. For nitrided samples, compared to TM8 and TV8 samples, as T_N increased, ratios of Mn^{4+} and V^{5+} with the highest valence state exhibited an increase at T_N = 400 °C. Moreover, the ratio of TiO_x decreased and the ratio of TiO_2 increased, even though NH_3 exhibited good reducibility. Data could be well interpreted as follows: O_v was occupied by N along with adsorbed O, possibly in the form of neutral NO radical and NO_2^{2-} radical ion. Till date, these phenomena have not been reported experimentally, which are important to understand the mechanism for photocatalytic performance of Mn-, V-, N-, and self-doped TiO_2.

1. Introduction

Titanium dioxide (TiO_2), a benchmark photocatalyst which shows the advantages of high efficiency, non-toxicity, chemical stability, and low-cost, has attracted extensive attention due to its potential applications in degradation of organic pollutants [1–6], photo energy conversion or water splitting [7], and self-cleaning [8–10]. However, TiO_2 can work effectively only under the ultraviolet (UV) light because the band gap energy of anatase TiO_2 is 3.2 eV (387 nm). One of the most effective ways to develop visible-light driven photocatalysts is to create impurity levels in the forbidden band of TiO_2 through the heteroatom doping, such as metal ion doping at Ti^{4+} sites [11] and non-metallic element doping at O^{2-} sites [12–15], and Ti^{3+} and/or oxygen vacancy (O_v) self-doping through the reduction reaction [16].

Till date, several attempts have been made to improve the photocatalytic performance of TiO_2 via doping of the metal ions with different dopant type, concentration, and oxidation state; however they did not provide unifying results and explanations. For example, transition metals cobalt (Co)-, chromium (Cr)-, copper (Cu)-, iron (Fe)-, molybdenum (Mo)-, vanadium (V)- and tungsten (W)-doped TiO_2 reduces the photoactivity of TiO_2 with the exception of W and the photoactivity of the powders roughly decreases according to the following sequence: $TiO_2/W > TiO_2/Mo > TiO_2/Cu > TiO_2/Fe \sim TiO_2/Co > TiO_2/V > TiO_2/Cr$ [17]. Somewhat differently, it was reported that V-, manganese (Mn)-, Fe-, Cu-, cerium (Ce)-, and W-doped TiO_2 powders exhibited photocatalytic activity in the order of $Fe/TiO_2 > Cu/TiO_2 > V/TiO_2 > W/TiO_2 > Ce/TiO_2 > Mn/TiO_2$. Among them, the Fe, Cu, and V ions improved the activity, while the W, Ce, and Mn ions led to detrimental effects, which were attributed to their energy levels, coordination numbers, and electronegativity [18]. Furthermore, the V ion has been believed to be the most effective in enhancing the photocatalytic activity of TiO_2 because of the enhanced absorption in the visible light region [19,20]. In contrast, it was also reported that the presence of V ion as a dopant did not affect the band gap energy of TiO_2 [21]. Following are the possible reasons for these diverse results: (1) The ionic radii of these dopant ions are different from that of Ti^{4+} in TiO_2, leading to the lattice distortion and reduction in the crystallite size [20] which affect the photoreactivity. (2) The substitution of +5 valent element for Ti^{4+} in TiO_2 breaks the charge balance, resulting in the production of Ti^{3+} and simultaneously creating O_v which always couples with Ti^{3+} (in the form of TiO_x) [20]. Therefore, not only the dopant element, but also Ti^{3+} and O_v affect the

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photoreactivity synergistically. (3) The dopant type and oxidation state lead to a change in the position of energy level in the forbidden band. According to the energy level diagram, it has been reported that V^{4+}, Mn^{3+}, and Co^{3+} can act as both hole and electron traps, while Fe^{3+}, Cr^{3+}, and Ni^{2+} can serve only as hole traps, and consequently these dopant ions play a different role in the photoreactivity. However, even though both Fe^{3+} and Cr^{3+} have similar energy levels in the TiO_2 lattice (0.2–0.4 eV above the valence band edge), their effects on the photocatalytic performance are substantially different. Therefore, it was suggested that the different electronic configurations might be responsible for the observed photoreactivities. Moreover, it was also noticed that all the dopants with d^5 (Fe^{3+}, Ru^{3+}, and Os^{3+}) and d^1 configurations (V^{4+} and Mo^{5+}) enhanced the photoreactivity [22]. In general, the photoreactivity of doped TiO_2 appears to be a complex function of the dopant concentration, energy level within the TiO_2 lattice, d-electronic configurations, and oxidation states, which undeniably deserve more detailed investigation.

In the present study, the dopant type (Mn or V) and concentration (2%) were fixed in order to reduce the changeable variables as much as possible. Mn and V were selected as the dopants because they have the multiple valences. The chemical states (CSs) of dopant (Mn and V) and Ti and O in TiO_2 were changed through reduction in the H_2/N_2 mixture gases followed by nitridation in NH_3 at different temperatures rather than through the substitution of different metal ions such as Ni^{2+}, Fe^{3+}, Mo^{6+}, V^{5+}, and W^{6+} in order to investigate the effects of CS on the photoreactivity.

2. Experimental procedure

2.1. Synthesis of Mn- and V-doped TiO_2@Fe_2O_3

γ-Fe_2O_3 nanoparticles (NPs) were synthesized through the hydrothermal method as described in our previous study [16]. The process for the synthesis of Mn- and V-doped TiO_2@γ-Fe_2O_3 is as follows: manganese acetate ($MnC_4H_6O_4$, 32 mg, 98%) and potassium permanganate ($KMnO_4$, 19 mg, 99.5%) were dissolved in deionized water (50 mL) with magnetic stirring at room temperature for 24 h to form the solution A. Then, γ-Fe_2O_3 NPs (200 mg) and citric acid ($C_6H_8O_7{\cdot}H_2O$, 1.2 g, 99.5%) were dispersed in isopropyl alcohol (170 mL, 99.7%) with ultrasonic treatment along with stirring for 10 min to form solution B. Next, diethylenetriamine (DETA, 0.06 mL, 99%) and titanium isopropoxide (TIP, 4.67 mL, 95%) were added dropwise into the solution B with vigorous stirring to form the solution C. After that, the solution A was added into the solution C, and subsequently isopropyl alcohol solution (150 mL, 80 vol%) was added into the mixed solution with stirring at room temperature for 1 h. The solution was then transferred into the 60 °C thermostat water bath with mechanical stirring (400 r min^{-1}) until gel was formed. The gel was finally dried at 80 °C for 12 h and then sintered at 450 °C for 2 h in air to obtain the Mn-doped TiO_2@γ-Fe_2O_3, hereafter denoted as the TM sample.

The V-doped TiO_2@γ-Fe_2O_3 sample (denoted as TV) was synthesized by following the procedure similar to that for the TM sample, except that the solution A was formed by dissolving ammonium metavanadate (NH_4VO_3, 35 mg, 99%) in deionized water (50 mL) and the pH was tuned to 2 with the hydrochloric acid solution (12 vol%).

2.2. Reduction and nitridation of Mn- and V-doped TiO_2@Fe_2O_3

The TM (TV) sample was, respectively, reduced in the H_2/N_2 flow (96%N_2 + 4%H_2, 500 sccm) at 400, 500, 600, 700, and 800 °C for 4 h, and the resulting samples were referred to as TM4 (TV4), TM5 (TV5), TM6 (TV6), TM7 (TV7), and TM8 (TV8), respectively. Then the TM8 and TV8 samples were, respectively, nitrided in the NH_3 flow (200 sccm) at 400, 500, 600, and 700 °C for 2 h, and the resulting samples were denoted as TM8N4 (TV8N4), TM8N5 (TV8N5), TM8N6 (TV8N6), and TM8N7 (TV8N7), respectively. The synthesis process is illustrated in Scheme 1.

2.3. Characterization

The crystal structure of the samples was determined by X-ray diffraction (XRD) using an X-ray diffractometer (SmartLab 9 kW, Rigaku Industrial Corporation, Osaka, Japan) with Cu Kα radiation (λ = 1.5406 Å) in the scanning range 10–80° and with a step size of 0.04°. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific ESCALAB 250Xi (Thermo Scientific Inc., USA). Magnetic measurements were carried out using a superconducting quantum interference device PPMS system (SQUID, PPMS EC-II, Quantum Design Inc., San Diego, California, USA). The photocatalytic activity was evaluated by the degradation of methylene blue (MB), which was illuminated by a xenon lamp (300 W) at a distance of 10 cm. Experimental procedure was as follows: aqueous solution of MB (100 mL, 10 mg L^{-1}) was mixed with magnetic catalysts (50 mg) in a vessel. Before the irradiation, the mixed solution was stirred in a dark condition for 60 min until an adsorption–desorption equilibrium was established. Samples of solution were extracted every 10 min from the reactor and the concentration of MB was analyzed using an ultraviolet–visible (UV–vis) spectrometer (UV-3200S, MAPADA, Shanghai, China) and calculated by using a calibration curve.

3. Results and discussion

3.1. Reduced samples

3.1.1. Variation of crystal structure with the reducing temperature (T_R)

Fig. 1 shows the XRD patterns of TM and TM4–TM8 samples. In the TM sample, TiO_2 crystallizes into anatase and rutile phases, according to their standard powder diffraction files (PDF) (Nos. 21-1272 and 21-1276), and the diffraction peak of anatase TiO_2 is stronger than that of rutile TiO_2. With the increase in T_R, the fraction of the rutile TiO_2 phase (f_R) increases; which can be calculated according to the following equation [23]: $f_R = (1 + 0.81I_A/I_R)^{-1}$, where I_A and I_R are the intensities of the most intense diffraction peaks of anatase and rutile TiO_2 phases, respectively. f_R is 0.42, 0.43, 0.51, and 0.89, respectively, for the samples TM, TM4, TM5, and TM6, and it becomes 1.0 for samples TM7 and TM8.

The magnetic core in the TM sample can be indexed to mixture phases of the α-Fe_2O_3 (PDF No.33-0664) and γ-Fe_2O_3 (PDF No. 39-1346), while it exhibits the mixture phases of α-Fe_2O_3, γ-Fe_2O_3, and α-Fe (PDF No. 06-0696) in the TM4 sample. When T_R exceeds 400 °C, the magnetic core gets completely transformed into α-Fe phase.

With the increase in T_R to 500 °C, a new phase of hexagonal ilmenite $FeTiO_3$ with the space group R-3(148) (PDF No. 29-0733) was produced. Its diffraction intensity suddenly decreased at T_R = 600 °C, indicating that $FeTiO_3$ was unstable in the H_2 atmosphere which resulted in its probable decomposition into TiO_2 and ferrite which was further reduced to Fe.

Fig. 2 depicts the XRD patterns of TV and TV4–TV8 samples. The structural evolution with increasing T_R behaves similar to that for the Mn-doped samples as shown in Fig. 1. However, compared to Fig. 1, the spectral features of V-doped samples show the following differences: (1) In the TV sample, the diffraction intensity of rutile TiO_2 is larger than that of anatase TiO_2. This indicates that V dopant in the TiO_2 lattice facilitates the formation of rutile phase. The fraction of rutile phase, f_R, is 0.61, 0.62, 0.74, 0.95, 1.0, and 1.0 for samples TV and TV4–TV8, respectively. (2) The diffraction intensities of both anatase and rutile TiO_2 phases in Fig. 2 are weaker than those in Fig. 1, indicating the smaller crystallite size in the V-doped samples. The ionic radius of V^{5+} is 0.54 Å, whereas that of Ti^{4+} is 0.68 Å. The crystal lattice gets distorted due to the substitution of Ti sites by V ions, consequently reducing the crystallite size [20]. (3) The diffraction peaks of V-doped TiO_2 slightly shift to larger 2θ angles, compared to those of the Mn-doped