Research Article

Photocatalytic Oxidation of Gaseous Isopropanol Using Visible-Light Active Silver Vanadates/SBA-15 Composite

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Received 1 July 2011; Revised 2 October 2011; Accepted 3 October 2011

Academic Editor: Jae Sung Lee

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An environmentally friendly visible-light-driven photocatalyst, silver vanadates/SBA-15, was prepared through an incipient wetness impregnation procedure with silver vanadates (SVO) synthesized under a hydrothermal condition without a high-temperature calcination. The addition of mesoporous SBA-15 improves the formation of nanocrystalline silver vanadates. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) confirms the presence of Bronsted and Lewis acids on the SVO/SBA-15 composites. The results of photoluminescence spectra indicated that the electron-hole recombination rate has been effectively inhibited when SVO was loaded with mesoporous SBA-15. All the composites loaded with various amounts of SVO inherit the higher adsorption capacity and larger mineralization yield than those of P-25 (commercial TiO2) and pure SVO. The sample loaded with 51% of SVO (51SVO/SBA-15) with mixed phases of Ag4V2O7 and α-Ag3VO4 exhibits the best photocatalytic activity. A favorable crystalline phase combined with high intensities of Bronsted and Lewis acids is considered the main cause of the enhanced adsorption capacity and outstanding photoactivity of the SVO/SBA-15 composites.

1. Introduction

Semiconductor photocatalysts have been studied extensively for degradation of organic compounds or water splitting [1–3]. Among semiconductor photocatalysts, titanium dioxide (TiO2) is the most widely employed. Due to the band gap, around 3.0 eV for rutile and 3.2 eV for anatase, TiO2 exhibits strong oxidation activity under ultraviolet (UV) light with a wavelength of 390 nm or less. Since UV light is only 3–5% of the solar spectrum, the photocatalytic activity of TiO2 is not enough under the visible and/or solar light irradiation. Therefore, numerous attempts have been made to improve TiO2 as a visible-light-active photocatalyst, including anion doping, cation doping, coupling of other semiconductor, and oxygen deficiency generation [4–6]. In addition, the degradation rate of TiO2 largely depends on the adsorption capacity which is associated with the specific surface area; therefore, a lot of research effort has been devoted to loading TiO2 species onto or incorporating them into the mesoporous silica SBA-15 to be a high-surface-area composite. SBA-15 material has extremely high surface area, large pore volume, and tunable pore size [7]. The motivation of TiO2/SBA-15 composite is that the dispersion and stabilization of the TiO2 species on a high surface area support leads to the synergistic effect with adsorptive and photocatalytic ability [8–10]. However, there are some basic restrictions using titania-SBA-15 composites as the visible-light-driven photocatalysts. First, TiO2 has low photo efficiency under visible-light illumination due to its wide band gap. Second, the most general method for synthesizing TiO2 is the sol-gel method, which requires high-temperature calcination (673 K or higher) to obtain good crystallinity. In recent years, Ag2ZnGeO4 [11], Ag3VO4 [12], and BiVO4 [13] were found to be effective as the visible-light active photocatalysts for water splitting and pollutant decomposing under visible-light illumination. These photocatalysts were prepared by hydrothermal synthesis method since this method offers many advantages, such as controllable particle size, high degree of crystallinity, and high purity.
while using milder synthesis temperatures and simpler process configurations.

The present work demonstrates the preparation of silver vanadate/SBA-15 composites (SVO/SBA-15) via hydrothermal synthesis using a postsynthesis step without high-temperature calcination. Photodecomposition of isopropanol (IPA) was selected as a model reaction to evaluate the photocatalytic performance of silver vanadate/SBA-15 composites since IPA is frequently detected in indoor and industrial air analyses. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), a very powerful technique to provide a high sensitivity and to allow the tracking of variations in the composition occurring in seconds, was used to identify reaction intermediates and to monitor the progress of the photocatalytic processes on the composite surface.

2. Experimental Procedure

2.1. Preparation of Photocatalyst. SBA-15 was synthesized with Pluronic P123 (EO20PO70EO20, Mw = 5800; Aldrich) and tetraethylorthosilicate (TEOS) according to a previous report [14]. Briefly, 4.0 g of P123 was dissolved in 30 g of deionized water and 120.0 g of HCl solution (2 M) with stirring at 313 K for 2 h. Then, 8.5 g of TEOS was added into the P123 solution, which was stirred for another 22 h until a white gel precipitated. The gel was transferred to a Teflon bottle and heated at 373 K for 24 h. The precipitate was filtered, washed several times with deionized water, dried overnight at 373 K, and then calcined at 773 K (heating rate of 1 K/min) for 4 h in air.

The silver-vanadate-loaded SBA-15 (SVO/SBA-15) was prepared via the incipient wetness impregnation procedure. In the preparation process, 0.204 g AgNO3 was dissolved in urea aqueous solution (120 g H2O, 0.577 g urea) with stirring at room temperature for 0.5 h to obtain solution A. Solution B was prepared by mixing 0.047 g NH4VO3 with 0.3 g SBA-15 in deionized water at 343 K for 1 h under an ultrasonic bath. A suspension formed when solution A was added dropwise to solution B under vigorous stirring for 1 h. The molar composition of the suspension AgNO3/NH4VO3/CO(NH2)2 was 3.0/1.0/12.0. The suspension was titrated to pH 7 using ammonia solution, followed by additional stirring at room temperature for 24 h. Finally, the as-obtained suspension was transferred into a Teflonlined autoclave with hydrothermal treatment (temperature: 413 K, time: 4 h). After the hydrothermal procedure, the resulting precipitates were collected and washed with deionized water three times and then dried at 353 K for 12 h. The samples were named as xSVO/SBA-15, where x was the amount of SVO loading by weight. The sample synthesized under identical conditions without the addition of SBA-15 was denoted SVO. The experimental procedure for preparing SVO/SBA-15 composites using incipient wetness impregnation is schematically shown in Scheme 1.

2.2. Sample Characterization. The X-ray diffraction (XRD) patterns of the powders were measured using an X-ray diffractometer (PANalytical X’Pert PRO) with Cu radiation (λ = 0.15418 nm) in the 2θ range of 20 to 60°. High-resolution transmission electron microscopy (HRTEM) images of the samples were observed on a Philips Tecnai G2 F20 microscope equipped with energy-dispersive X-ray spectroscopy (EDX) operated at an accelerating voltage of 200 kV. Photoluminescence (PL) spectra were recorded by a fluorescence spectrophotometer (Dongwoo Optron) at 1 atm and 25°C. In situ DRIFTS measurements were performed using a PerkinElmer FTIR spectrometer (Spectrum GX) and a diffuse reflectance accessory (Harrick Scientific, DRP-PE9) with a temperature- and atmosphere-controlled high-temperature low-pressure reaction cell (Harrick Scientific, HVC-DRP-3). To determine the types of acid site present on the samples, temperature-programmed desorption of ammonia (NH3) was carried out using DRIFT. Ammonia usually provides the probe molecules in spectroscopic experiments to determine the type of acid site in heterogeneous catalysis: Bronsted sites or Lewis sites. Prior to the experiments, the samples were heated in situ from room temperature to 523 K at 10 K/min in N2 flow (30 mL/min), held at 523 K for 30 min, and then cooled down to 303 K. The samples were saturated at 303 K with a gas mixture of 5% NH3 in N2 (30 mL/min) for 30 min. At the end of the saturation process, the samples were flushed with N2 flow (30 mL/min). Then, the samples were heated again at a heating rate of 10 K/min from 30 K to 523 K and held at 523 K for 60 min. The DRIFT spectra with a resolution of 4 cm⁻¹ were collected in the interval of 1200–1700 cm⁻¹ for determining surface acidity [12]. The surface area and pore volume of the as-prepared samples were determined using a volumetric sorption analyzer (Micromeritics ASAP 2020). The samples were degassed at 473 K under vacuum conditions for a period of at least 4 h prior to measurements. The nitrogen adsorption/desorption isotherms were measured over a relative pressure (P/P0) range of approximately 10⁻³ to 0.995. The surface areas were calculated using the Brunauer-Emmett-Teller ( BET) method in the relative pressure range of 0.06–0.2. The pore size distributions were determined from the analysis of the adsorption isotherm using the Barret-Joyner-Halenda (BJH) algorithm. The total pore volumes were estimated from the adsorbed N2 amount at P/P0 = 0.973.

2.3. Photocatalytic Activity Evaluation with MS and DRIFTS. The photocatalytic oxidation of IPA was performed in situ in an IR cell with ZnSe windows. An LED lamp, with a wavelength ranging from 430 to 620 nm with a photon intensity of 4 mW/cm², was used as the visible-light source [13]. A gaseous IPA/O2 mixture was generated, corresponding to the target IPA concentration of 610 ppmv. Prior to the experiments, the samples were pretreated by heating and flushing with N2 flow (20 mL/min) from room temperature to 523 K, held at 523 K for 30 min, and then cooled to 303 K. The procedure for all PCO experiments was as follows: (1) IPA/O2 flow was introduced into the photoreactor at a constant flow rate of 10 mL/min; (2) when the photoreactor inlet and outlet IPA concentrations were approximately equal, the LED lamp was turned on, and the IPA/O2 flow was stopped; (3) the photoreactor was flushed with the O2 flow at 10 mL/min during
PCO experiment. To verify the gaseous composition (intermediate), the samples were monitored online with a quadrupole mass spectrometer (MS, SRS QMS300) at regular intervals. The spectra of the adsorbed species on the catalyst surface were recorded under both darkness and illumination. The spectra of the catalyst and the reaction intermediates during the reaction were expressed in units of Kubelka-Munk (K-M).

3. Results and Discussion

3.1. Characterization of Samples. The X-ray powder diffraction patterns of the SVO and three SVO/SBA-15 samples are shown in Figure 1. The SVO/SBA-15 composites have two kinds of XRD patterns, assigned to the pure α-Ag₃VO₄ (JCPDS 43-0542) for 17SVO/SBA-15 and 34SVO/SBA-15 samples and to the mixed phases of Ag₄V₂O₇ (JCPDS 77-0097) and α-Ag₃VO₄ for 51SVO/SBA-15, respectively. The bulk SVO had the same crystalline structure with 51SVO/SBA-15. Figure 2 shows the adsorption-desorption isotherms of SBA-15 and SVO/SBA-15 samples. According to the IUPAC classification of adsorption isotherms, the isotherms of SBA-15 and SVO/SBA-15 can be classified as type IV which is a typical indication of mesoporous materials. With increasing the SVO loading, the SVO/SBA-15 sample gives isotherm with similar inflection but with reduced sharpness and a shift to higher relative pressure, indicating an increase of the pore diameter when SVO was loaded into/onto SBA-15. The sharpness of the steeps is decreased as the amount of SVO increases, indicating that the pore size distribution becomes broad with an increase of SVO amount in the SBA-15 framework. The textural properties of SBA-15 support and SVO/SBA-15 samples are listed in Table 1. It can be seen that the specific surface area and pore volumes of SVO/SBA-15 samples significantly decrease with increasing silver vanadate loading, whereas the pore diameter increases. When the SVO/SBA-15 samples were synthesized using a postsynthesis method, the silver and vanadate species reacted on the surface of SBA-15; thus, the BET surface and pore volumes of SVO/SBA-15 composites decreased with increasing amount of SVO. The average pore diameter increased for SVO/SBA-15, which might be due to the small pores of SBA-15 being obstructed by silver vanadate nanoparticles. Direct evidences from TEM images can be used to confirm the formation of SVO nanocrystals on the SBA-15. Figure 3 shows the TEM images of SBA-15 and 51SVO/SBA-15, which are viewed along the <110> orientations. The TEM image of SBA-15 (Figure 3(a)) clearly shows well ordered cylindrical channels, indicative of 2D hexagonal p6mm mesostructure. Nevertheless, the surfaces of 51SVO/SBA-15 (Figure 3(b)) seemed like to be covered by clouds which were caused by aggregation of the SVO particles on the surface of SBA-15. The micrograph result indicates that high loading of nanocrystalline SVO can be well dispersed inside the mesoporous channels of the SBA-15 using urea as the chelating agent, which exhibits a strong interaction between urea and metal ions and prevents the precipitation of silver and vanadium ions before the formation of silver vanadates-silica composites.
The IPA bands decreased progressively for all SVO/SBA-15 composites; however, a slight reduction of IPA was observed for P25. Moreover, new features at about 1703, 1571, 1425, 1371, and 1241 cm\(^{-1}\) were developed for all samples. The peak at 1571 cm\(^{-1}\) is clearly visible, which is associated with the \( \nu_{(COO)} \) (COO) mode of formate, while new bands at 1703, 1425, 1371, and 1241 cm\(^{-1}\) are attributed to acetone. From the spectra distribution, FTIR results have indicated that IPA adsorbed under illumination can be degraded to acetone and to formate, the intermediate species adsorbed on the surface of the photocatalysts. The adsorption and photodegradation curves of gaseous IPA during visible-light irradiation were shown in Figure 5. The concentration of gaseous IPA, determined using a quadrupole MS, rapidly decreased during the initial 10 min, which was due to the adsorption of IPA on the catalyst surface. After 30 min, the concentration of gaseous IPA returned to the initial state, indicating that the adsorption of IPA reached equilibrium. In the absence of irradiation, the as-prepared SVO/SBA-15 composites exhibited much higher adsorption capabilities of IPA than those of SVO and P-25. The adsorption capability of the samples decreased as the following order: 51SVO/SBA-15 > 34SVO/SBA-15 > 17SVO/SBA-15 > SVO > P-25. It is well known that photocatalytic degradation of organic pollutants follows Langmuir-Hinshelwood kinetics [16]; the L-H model can be simplified to a pseudo-first-order expression: \( \ln(C_e/C) = kt \) (where \( C_e \) and \( C \) are the equilibrium concentration of adsorption and the concentration of VOC at the exposure time, \( r \), resp., and \( k \) is the apparent rate constant). The calculated \( k_{app} \) of IPA decreased in the order: 17SVO/SBA-15 (0.048 min\(^{-1}\)) > 34SVO/SBA-15 (0.045 min\(^{-1}\)) > P25 (0.029 min\(^{-1}\)). For the initial stage of photodegradation reaction, the composite materials (17SVO/SBA-15 and 34SVO/SBA-15) with \( \alpha \)-Ag\(_3\)VO\(_4\) crystalline had stronger initial photoactivity than that of mixed structures of \( \alpha \)-Ag\(_3\)VO\(_4\) and Ag\(_x\)V\(_2\)O\(_7\) (51SVO/SBA-15). Only the decrease of the IPA concentration in the early stage is not sufficient for the comparison of photocatalytic activity; therefore, the amount of CO\(_2\), a final product of IPA photodegradation, was measured in Figure 5.
decomposition product of gaseous IPA, was measured to evaluate the long-term photoactivity of all samples. The mineralization yield of gaseous IPA is defined as [4]

\[
\text{Mineralization} \%(\%) = \frac{1/3 [\text{CO}_2]_{\text{production}}}{[\text{CH}_3\text{CHOHCH}_3]_{\text{original}}} \times 100\%.
\]

For a 100% mineralization yield, three moles of carbon dioxide are formed from each mole of IPA. Figure 6 represents the CO\(_2\) concentrations of various samples; after visible-light irradiation for 270 min, the CO\(_2\) concentrations of SVO/SBA-15 composites are much higher than those of SVO and P25. The mineralization yields of IPA were 60%, 55%, 50%, 46%, and 44% for 51SVO/SBA-15, 34 SVO/SBA-15, 17 SVO/SBA-15, SVO, and P25, respectively. When the mass ratio of silver vanadates to SBA-15 is small (17SVO/SBA-15), each nano silver vanadates particle is surrounded by a larger amount of mesoporous silica, which leads to the increase of the average distance from the adsorption sites to the photocatalytic sites, bringing about a decrease of the mineralization yield. Generally speaking, the photocatalytic activity is strongly related to the crystalline phase. Konta et al. [17] reported that \(\alpha\)-Ag\(_3\)VO\(_4\) has stronger photocatalytic activity than those of \(\beta\)-AgVO\(_3\) and Ag\(_4\)V\(_2\)O\(_7\) for oxygen production from water splitting under visible-light irradiation. In this study, it was observed that the 51SVO/SBA-15 sample, with mixed phases of Ag\(_4\)V\(_2\)O\(_7\) and \(\alpha\)-Ag\(_3\)VO\(_4\), exhibits the highest
3.3. Correlation between Photocatalytic Activity and SBA-15 Support. From Figures 4 and 5, the adsorption of gaseous IPA on sample surface is highly relevant to the contents of silver vanadate in SVO/SBA-15 composites. In the absence of irradiation, the composite samples exhibit a much higher adsorption capability of gaseous IPA than those of P25 and bulk SVO, which is attributed to their much higher specific surface area and pore volumes than P25 and bulk SVO. However, the adsorption of gaseous IPA showed different trends relative to the specific surface area of composite.

mineralization yield, whereas 34SVO/SBA-15 has low mineralization yield even though it has a high crystallinity of α-Ag3VO4.

17SVO/SBA-15 has the highest specific surface area of 217 m²g⁻¹ but its adsorption capability for gaseous IPA was lower than those of 34SVO/SBA-15 and 51SVO/SBA-15 samples. This phenomena is quite different with other studies, which have shown that the much higher specific surface area and pore volume of TiO₂-containing mesoporous silica composites compared to those of pure titania are beneficial for the adsorption of organic pollutants [18–20]. Therefore, parameters other than surface area need to be investigated. It is well known that the adsorption capacity is mainly determined by the specific surface area and nature of the surface of the photocatalyst. As shown in Figure 5, 51SVO/SBA-15 exhibited the highest adsorption capacity of IPA instead of 17SVO/SBA-15. However, 17SVO/SBA-15 had much higher
specific surface area and pore volume than those of SVO/SBA-15, implying that a large surface area may not be beneficial to the adsorption capability in case of composite materials. Therefore, the IPA adsorption capacity is thus greatly influenced by the nature of the surface of SVO, rather than the specific surface area. To further characterize the surface attributes that affect IPA adsorption, the surface acidity, the existence of Brønsted and Lewis acid sites, of the samples was examined using DRIFTS to detect ammonia adsorption on the photocatalysts surface. A literature survey indicates that IR spectroscopic studies of ammonia adsorbed on solid surfaces have made it possible to distinguish between Brønsted and Lewis acid sites of a catalyst [21–26]. Before the DRIFT measurements, the samples were saturated with NH\textsubscript{3}/N\textsubscript{2}, flushed with N\textsubscript{2} flow to remove physically adsorbed ammonia, and then heated from 303 K to 523 K. The intensity of chemisorption was determined based on the irreversible adsorption of ammonia. Figure 7 shows the IR spectra of ammonia adsorbed onto SVO and SVO/SBA-15 samples which were heated at 523 K for 30 min. The existence of NH\textsubscript{4} ions adsorbed onto Brønsted acid sites of the silver vanadate surfaces is supported by the presence of a band at 1425 cm\textsuperscript{-1} due to the asymmetric deformation mode [21–23]. The band at 1604 cm\textsuperscript{-1} is assigned to NH\textsubscript{3} coordinately bonded to Lewis acid sites [24–26]. It can be concluded that both Brønsted and Lewis acid sites exist on the surfaces of SVO and SVO/SBA-15. The intensities of Brønsted and Lewis acid sites, detected at 1425 and 1604 cm\textsuperscript{-1}, respectively, follow the sequence: 51SVO/SBA-15 > 34SVO/SBA-15 > 17SVO/SBA-15 ~ SVO. The trend of Brønsted and Lewis acid sites is in agreement with that of the adsorption capacity. That is, higher intensities of Brønsted and Lewis acids of silver vanadates indicate a larger adsorption capacity for IPA.

3.4. Photoluminescence Spectra. In this study, photoluminescence spectra were measured to disclose the migration, transfer, and recombination processes of the photogenerated electron-hole pairs of all samples. For the PL intensity measurements, the same amount of sample was used. As shown in Figure 8, the photoluminescence (PL) intensity of these samples decreases in the order of P25 > SVO > 17SVO/SBA-15 > 34SVO/SBA-15 > 51SVO/SBA-15. The PL of SVO/SBA-15 composites show obvious decrease in the intensity of PL spectra as compared to SVO, indicating the recombination of photoelectrons and holes is efficiently suppressed in the composite semiconductors. Moreover, the resulting 51SVO/SBA-15 composite shows much lower intensity of PL spectra than those of 17SVO/SBA-15 and 34SVO/SBA-15. However, the active SVO content of 51SVO/SBA-15 is much higher than those of the others. Therefore, the intensity of PL spectra of composite decreased with increasing SVO content. As shown in Figure 3, the TEM micrograph result indicates that high loading of nanocrystalline SVO can be well dispersed inside the mesoporous channels of the SVO/SBA-15. The reduction of PL intensity seems to depend on the amount of nanosized SVO rather than SBA-15, an insulator. It is suggested that the intensity of photoluminescence spectra corresponds to the recombination rates of the holes formed in the O\textsubscript{2p} band and the electron in the V\textsubscript{3d} band. The slower recombination process of photogenerated charges (the less the PL intensity) can facilitate the enhancement of photocatalytic activity of SVO/SBA-15 composite.

4. Conclusion

In this study, the presence of nanoscaled silver vanadates significantly promoted the adsorption capacity and photocatalytic activity. XRD and TEM results indicate the nanosized α-Ag\textsubscript{3}VO\textsubscript{4} for 17 and 34SVO/SBA-15 and to the mixed phases of Ag\textsubscript{4}V\textsubscript{2}O\textsubscript{7} and α-Ag\textsubscript{3}VO\textsubscript{4} for 51SVO/SBA-15 and that SVO dispersed well in the channels or on the surface of SBA-15 without affecting the SBA-15 mesoporous structure, respectively. The DRIFT spectra identify the formation of intermediates, formate and acetone, on the surface of SVO/SBA-15.
composites. The composite photocatalyst exhibits highly enhanced photocatalytic activity under visible-light irradiation, and the highest efficiency is for the 51SVO/SBA-15 composite. A favorable crystalline phase and the reduction of the recombination of photogenerated hole-electron pairs are responsible for the enhanced adsorption capacity and high mineralization yield of SVO/SBA-15 composites.

Acknowledgment

The authors are grateful to the National Science Council of Taiwan (Grant no. NSC 99-2221-E-168-027), for supporting this study.

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