Investigations on the Phase Transition between CdV$_2$O$_6$ and Cd$_2$V$_2$O$_7$ and Their Photocatalytic Performances

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CdV$_2$O$_6$ and Cd$_2$V$_2$O$_7$ were successfully synthesized by a simple hydrothermal process. The effects of the hydrothermal temperature and pH on the phase transition between CdV$_2$O$_6$ and Cd$_2$V$_2$O$_7$ were investigated in detail. That the Cd$_2$V$_2$O$_7$ phase could transform into CdV$_2$O$_6$ was attributed to polymerization of vanadate in an acidic environment as the V/O ratio increased as the pH decreased. V$_2$O$_7^{4-}$ was stable in a neutral or alkaline environment at an identical hydrothermal temperature, therefore, the Cd$_2$V$_2$O$_7$ phase was obtained after hydrothermal treatment for 24 h. Because the degree of hydrolysis of NH$_4$Cl increased with increasing temperature in the solution, the increased temperature accelerated the speed of the pH decrease. Therefore, the hydrothermal temperature played an important part in the phase transition between CdV$_2$O$_6$ and Cd$_2$V$_2$O$_7$. Cd$_2$V$_2$O$_7$ and CdV$_2$O$_6$ showed high photocatalytic activity for the degradation of methylene blue under visible-light irradiation.

Introduction

Complex vanadium(V) oxides have received renewed interest as electrode materials and catalysts.[1–13] According to a previous theoretical study, the V 3d orbital is usually located below the analogous d orbitals of other transition metals in the energy spectrum, and, therefore, the bottom conduction band is lowered to a more positive position.[14] Accordingly, vanadium is an important candidate element for visible-light photocatalysts. Some vanadium-containing oxides, such as BiVO$_4$ and InVO$_4$, have been developed successfully as visible-light photocatalysts for O$_2$ and H$_2$ evolution in the presence of the sacrificial reagents AgNO$_3$ and CH$_3$OH, respectively.[15,16] Recently, Wang and co-workers found that Zn$_3$V$_2$O$_7$ had photocatalytic activity for O$_2$ evolution under visible-light irradiation.[17] Zhu and co-workers have investigated the hierarchical nanostructure of Zn$_3$V$_2$O$_7$(OH)$_2$(H$_2$O)$_2$ with flowerlike and nanobelt morphologies and converted the Zn$_3$V$_2$O$_7$(OH)$_2$(H$_2$O)$_2$ precursors into porous Zn$_3$V$_2$O$_6$.[18] They found that the photocatalytic activities were significantly improved when Zn$_3$V$_2$O$_8$ had a flower-shaped superstructure. However, work concerning the phase transition between CdV$_2$O$_6$ and Cd$_2$V$_2$O$_7$ under hydrothermal conditions has not been reported. No work has been reported on CdV$_2$O$_6$ and Cd$_2$V$_2$O$_7$ as photocatalysts. Therefore, there is a need to investigate the phase-transition mechanism of CdV$_2$O$_6$ and Cd$_2$V$_2$O$_7$ and their photocatalytic activity.

In this paper, CdV$_2$O$_6$ and Cd$_2$V$_2$O$_7$ were controllably synthesized by a simple hydrothermal method. The influence of the reaction parameters (pH and hydrothermal temperature) on the phase transition between CdV$_2$O$_6$ and Cd$_2$V$_2$O$_7$ and the relationship between the phases and photocatalytic activities were investigated. The formation of CdV$_2$O$_6$ and Cd$_2$V$_2$O$_7$ depended on the pH under identical hydrothermal temperatures. The hydrolysis of NH$_4$Cl played an important part in the formation of CdV$_2$O$_6$ and Cd$_2$V$_2$O$_7$ under different hydrothermal temperatures. CdV$_2$O$_6$ and Cd$_2$V$_2$O$_7$ showed highly efficient photocatalytic activities for the photocatalytic decomposition of methylene blue (MB).

Results and Discussion

Controlled Synthesis of CdV$_2$O$_6$ and Cd$_2$V$_2$O$_7$

The pH of the precursor precipitates had a crucial effect on the formation of CdV$_2$O$_6$ and Cd$_2$V$_2$O$_7$. The precursor suspensions were adjusted to the desired pH by adding NaOH and HCl solutions and then they were hydrothermally treated at 180 °C for 24 h. Figure 1 shows the XRD patterns of CdV$_2$O$_6$ and Cd$_2$V$_2$O$_7$ samples prepared by hydrothermal synthesis at different pH values. At pH 6, the diffraction peaks of all the samples were easily indexed as a pure, orthorhombic crystalline phase Cd$_2$V$_2$O$_7$, which is in good agreement with the standard card (JCPDS Card...
number: 20-0189). At pH 7 or 8, the product was pure Cd$_2$V$_2$O$_7$, which was in good agreement with the standard card (JCPDS Card number: 78-0951). At pH 9 or 5, products that contained other phase were obtained. The microstructures of the as-prepared samples were investigated with scanning electron microscopy (SEM). Figure 2 (a) shows an SEM micrograph of CdV$_2$O$_6$ prepared at pH 6, from which one can see that the sample is made up of short, thick rods. At pH 7 and 8, particles were observed in the SEM micrograph of Cd$_2$V$_2$O$_7$ (Figure 2, b–d), and it appeared that the particles increased in size as pH value increased.

### Formation Mechanism of CdV$_2$O$_6$ and Cd$_2$V$_2$O$_7$

The formation of CdV$_2$O$_6$ rods is a typical hydrothermal phase-transition process: a highly supersaturated solution was adopted, and hollow spherical particles acted as the precursor for the synthesis of crystalline Cd$_2$V$_2$O$_7$ particles. It appeared that the Cd$_2$V$_2$O$_7$ particles accumulated by self-assembly. At the beginning, the direct mixing of the two solutions at pH 6 led to the formation of a lot of hollow spherical particles (Figure 3). Upon hydrothermal treatment, the Cd$_2$V$_2$O$_7$ phase transformed to α-CdV$_2$O$_6$, which is in good agreement with the standard card (JCPDS Card number: 73-0187). The Cd$_2$V$_2$O$_7$ phase transformed to α-CdV$_2$O$_6$ because of the polymerization of vanadate in an acidic environment, and the V/O ratio increased as the pH decreased. Finally, the α-CdV$_2$O$_6$ phase transformed to CdV$_2$O$_6$, which means that CdV$_2$O$_6$ is the thermodynamically stable phase (Figure 4).

Conversely, Cd$_2$V$_2$O$_7$ grew by a simple hydrothermal ripening process. Initially, the direct mixing of the two solutions led to the formation of Cd$_2$V$_2$O$_7$ hollow spherical particles (Figure 3). At pH 8, the phases became a mixture. Upon hydrothermal treatment, the mixture transformed to a pure Cd$_2$V$_2$O$_7$ phase after 4 h (Figure 5). SEM images of a series samples treated at 180 °C for different durations are in accord with the XRD patterns; the Cd$_2$V$_2$O$_7$ particles appeared only after 4 h of hydrothermal treatment (Figure 6, a). The particle morphology appeared at the same time as the Cd$_2$V$_2$O$_7$ crystalline phase. Under hydrothermal treatment, the formation of tiny crystalline nuclei in a supersaturated medium occurred and was followed by crystal growth. Large particles grow at the cost of small ones because of the energy difference in the solubility between the large and small particles according to the well-known Gibbs–Thomson law. In the early stages, an examination of the intermediate samples showed the coexistence of irregular large particles and nanoparticles (Figure 6, b and c). As the reaction continued, the irregular nanoparticles disappeared, and the large particles increased in size, which suggests that the large particles grew at the cost of the small...
particles (Figure 6, d).\textsuperscript{[24,25]} The Cd\textsubscript{2}V\textsubscript{2}O\textsubscript{7} phase did not transform to CdV\textsubscript{2}O\textsubscript{6}. The Cd\textsubscript{2}V\textsubscript{2}O\textsubscript{7} phase was obtained after hydrothermal treatment for 24 h because V\textsubscript{2}O\textsubscript{7}\textsuperscript{4−} is stable in a neutral or alkaline environment under identical hydrothermal temperatures.

Effects of Temperature on the Formation of CdV\textsubscript{2}O\textsubscript{6} and Cd\textsubscript{2}V\textsubscript{2}O\textsubscript{7}

The hydrothermal temperature had a significant effect on the formation of CdV\textsubscript{2}O\textsubscript{6} and Cd\textsubscript{2}V\textsubscript{2}O\textsubscript{7}. Figure 7 shows XRD patterns of samples prepared at various hydrothermal temperatures at pH 6. The product was a mixture of CdV\textsubscript{2}O\textsubscript{6}, Cd\textsubscript{2}V\textsubscript{2}O\textsubscript{7}, and α-CdV\textsubscript{2}O\textsubscript{6} after treatment at 120 °C. The amount of CdV\textsubscript{2}O\textsubscript{6} formed increased with increasing temperature, and the Cd\textsubscript{2}V\textsubscript{2}O\textsubscript{7} and α-CdV\textsubscript{2}O\textsubscript{6} phases were transformed into CdV\textsubscript{2}O\textsubscript{6}. It appears that the hydrothermal phase-transition process from the CdV\textsubscript{2}O\textsubscript{6} rods occurs at 180 °C. This is attributed to the hydrolysis of NH\textsubscript{4}Cl, which is an endothermic reaction (ΔH > 0), and we can obtain the formula:

\[
\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

The hydrolysis constant \( K_0 \) increased with increasing temperature, so the degree of hydrolysis increased with increasing temperature. The H\textsuperscript{+} concentration increased with increasing temperature, which accelerates the rate of the decrease in pH. Therefore, the pure CdV\textsubscript{2}O\textsubscript{6} phase was obtained at 180 °C.

Figure 8 shows the XRD patterns of samples prepared at various hydrothermal temperatures at pH 8. At 240 °C, the Cd\textsubscript{2}V\textsubscript{2}O\textsubscript{7} phase began to transform into the CdV\textsubscript{2}O\textsubscript{6} phase. The transformation of the Cd\textsubscript{2}V\textsubscript{2}O\textsubscript{7} phase into the CdV\textsubscript{2}O\textsubscript{6} phase was also attributed to the hydrolysis of NH\textsubscript{4}Cl. As mentioned above, the hydrolysis constant \( K_0 \) increased with increasing temperature, so the degree of hydrolysis increased with increasing temperature. The concentration of H\textsuperscript{+} increased with increasing temperature. At 240 °C, the hydrothermal environment was acidic. Therefore, the Cd\textsubscript{2}V\textsubscript{2}O\textsubscript{7} phase began to transform to the CdV\textsubscript{2}O\textsubscript{6} phase.

Optical Properties and Photocatalytic Activity

The optical absorption of CdV\textsubscript{2}O\textsubscript{6} and Cd\textsubscript{2}V\textsubscript{2}O\textsubscript{7} was measured by using a UV/Vis spectrometer. Figure 9 shows typical diffuse reflection spectra (DRS) of CdV\textsubscript{2}O\textsubscript{6} and
Cd$_2$V$_2$O$_6$ obtained at different pH values. The steep shape of the spectra indicated that the visible-light absorption was not caused by a transition from the impurity level but was caused by the band-gap transition. The Cd$_2$V$_2$O$_6$ had a wider absorption range, which meant the Cd$_2$V$_2$O$_6$ could absorb more visible light. The optical absorption range of Cd$_2$V$_2$O$_6$ was wider than that of Cd$_2$V$_2$O$_7$ because the polymerization degree of vanadate increased as the pH decreased. The vanadate became darker, so the absorption range broadened. The band gap of the sample can be evaluated from the following equation: $\alpha(h\nu) = A(h\nu - E_g)^n$, in which $\alpha$, $n$, $E_g$, and $A$ are the absorption coefficient, light frequency, band-gap energy, and a constant, respectively. Among them, $n$ depends on the characteristics of the transition in a semiconductor. For Cd$_2$V$_2$O$_6$ and Cd$_2$V$_2$O$_7$, the value of $n$ is 1 for the direct transition. The band-gap energy ($E_g$) of the as-prepared sample can be thus estimated from a plot of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$). The intercept of the tangent with the x axis gives a good approximation of the band-gap energy for the sample. The inset of Figure 9 shows the plot of $(\alpha h\nu)^2$ vs. $h\nu$ calculated from the absorption spectrum. Finally, the band-gap energy of the Cd$_2$V$_2$O$_6$ and Cd$_2$V$_2$O$_7$ samples are shown in Table 1. The band-gap value of Cd$_2$V$_2$O$_6$ is much lower than that of Cd$_2$V$_2$O$_7$ because Cd$_2$V$_2$O$_7$ has a wider absorption range. The band-gap energy of Cd$_2$V$_2$O$_7$ obtained at pH 7 is higher than that of Cd$_2$V$_2$O$_7$ obtained at pH 8, because of the size effects of Cd$_2$V$_2$O$_7$.

\begin{table}[h]
\centering
\begin{tabular}{lccc}
\hline
Sample & Cd$_2$V$_2$O$_6$ & Cd$_2$V$_2$O$_7$ (pH 7) & Cd$_2$V$_2$O$_7$ (pH 8) \\
\hline
Band gap [eV] & 2.144 & 2.878 & 2.809 \\
\hline
\end{tabular}
\caption{The direct band gaps calculated from their corresponding absorption spectra for Cd$_2$V$_2$O$_6$ and Cd$_2$V$_2$O$_7$ treated at 180 °C.}
\end{table}

Methylene blue (MB) was used as a probe of the heterogeneous photocatalysis of the samples, and the decomposition could be monitored by the visible-light absorption signature. The characteristic absorption of MB at 664 nm was chosen as the monitored parameter for the photocatalytic degradation process. Figure 10 shows plots of the degradation of MB in the presence of Cd$_2$V$_2$O$_6$ and Cd$_2$V$_2$O$_7$ pH series samples. A first-order linear relationship was revealed by plots of ln($C/C_i$) vs. irradiation time ($t$); $C$ is the concentration of MB at the irradiation time $t$ and $C_i$ is the concentration in the adsorption equilibrium of the photocatalysts before irradiation. From the first-order linear fit, the determined reaction rate constants $k$ were 0.29842, 0.27441, and 0.29897 h$^{-1}$, respectively, for the Cd$_2$V$_2$O$_6$ and Cd$_2$V$_2$O$_7$ pH series samples. Among the Cd$_2$V$_2$O$_7$ pH series samples, the photocatalytic activity increased as the pH value increased. As confirmed by the XRD results, the crystallinity of the sample obtained at pH 7 was lower than that at pH 8. The higher crystallinity meant there were fewer defects in the as-synthesized sample. Lattice defects can act as recombination centers for photoinduced electrons and holes and, thus, significantly reduce the photocatalytic activity. However, the light absorption intensity also makes a key contribution to the photocatalytic activity. From the DRS spectra in Figure 9, Cd$_2$V$_2$O$_6$ shows much enhanced visible-light absorption intensity over that of Cd$_2$V$_2$O$_7$. However, the Cd$_2$V$_2$O$_7$ obtained at pH 8 had small crystals with a relatively larger reaction area. Therefore, the photocatalytic activity of Cd$_2$V$_2$O$_7$ obtained at pH 8 and Cd$_2$V$_2$O$_6$ was similar.

**Figure 9.** UV/Vis diffuse reflectance spectra of Cd$_2$V$_2$O$_6$ and Cd$_2$V$_2$O$_7$ treated at 180 °C. The inset shows the plots of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$).

**Figure 10.** First-order plots of the photocatalytic degradation of MB with samples synthesized at different pH values (squares: Cd$_2$V$_2$O$_6$, circles: Cd$_2$V$_2$O$_7$ obtained at pH 7, triangles: Cd$_2$V$_2$O$_7$ obtained at pH 8).

**Conclusions**

Cd$_2$V$_2$O$_6$ and Cd$_2$V$_2$O$_7$ were controllably synthesized by a simple hydrothermal method. With hydrothermal treatment, the Cd$_2$V$_2$O$_7$ phase was transformed to Cd$_2$V$_2$O$_6$; this was attributed to the polymerization of vanadate in an acid environment. As V$_2$O$_4^{2-}$ is stable in a neutral or alkaline environment under identical hydrothermal temperature, the Cd$_2$V$_2$O$_7$ phase could be obtained in neutral or alkaline environment. However, the Cd$_2$V$_2$O$_7$ phase began to transform to the Cd$_2$V$_2$O$_6$ phase in an alkaline environment at 240 °C. This is attributed to the hydrolysis of NH$_4$Cl. The photocatalytic properties of Cd$_2$V$_2$O$_6$ and Cd$_2$V$_2$O$_7$ were investigated under visible-light irradiation. It was found that Cd$_2$V$_2$O$_6$ and Cd$_2$V$_2$O$_7$ possessed a high catalytic activity towards the degradation of MB.
Experimental Section

Materials: Analytical reagent grade methylene blue was used without further purification. Other chemicals were commercial products of analytical grade or reagent grade. All solutions were prepared with distilled water.

Preparation of CdV₂O₆ and Cd₂V₂O₇: In a typical procedure, NH₄ClO₄ (4 mmol) was dissolved in deionized water (14 mL). Under vigorous agitation, an aqueous solution (14 mL) containing CdCl₂·2.5H₂O (2 mmol) was added to the above solution at room temperature. The pH value of the mixture was adjusted with 1 M NaOH and HCl (36%). The mixture was then transferred into a 40 mL Teflon-lined steel autoclave. The autoclave was heated under autogenous pressure at a series of temperatures for 24 h. The autoclave was cooled gradually to room temperature. The precipitate was washed with distilled water three times and then dried at 60 °C in air.

Characterizations: The degradation rates of methylene blue (MB) solutions were monitored with a Hitachi U-3010 spectrophotometer, and the maximum absorption wavelength of the MB solutions were identified as 664 nm. The UV/Vis spectra were recorded in the range 200–800 nm. The UV/Vis diffuse reflectance spectra (UV/Vis DRS) of the samples were obtained with a UV/Vis spectrophotometer (UV-3010, Shimadzu) equipped with an integrating-sphere accessory. BaSO₄ was used as a reference standard. The pH values were measured with a PHSJ-4A pH meter. XRD experiments were performed with a Rigaku DMAX-2400 diffractometer with Cu-Kα radiation. The size and morphologies of CdV₂O₆ and Cd₂V₂O₇ were characterized with the aid of a LEO-1530 field emission scanning electron microscope (SEM).

Photocatalytic Oxidative Degradation: The photocatalytic activities of CdV₂O₆ and Cd₂V₂O₇ were evaluated by the decomposition of MB under visible-light irradiation. A 50 W xenon lamp (>290 nm, Institute of Electric Light Sources, Beijing) was focused through a window, and a 420 or 450 nm cutoff filter was placed onto the cell window to ensure the desired irradiation conditions. The average light intensity was 40 mW/cm². The radiant flux was measured with a power meter (Institute of Electric Light Sources, Beijing).

A cylindrical double-layer glass photochemical reactor with internal diameter 70 mm, external diameter 80 mm, and height 80 mm was utilized for the photocatalysis reactions. A distance of about 12 cm between the lamp and reactor was maintained. Running water was piped into the layer to keep the temperature constant.

The photocatalytic degradation of MB in the aqueous solutions was studied by using CdV₂O₆ or Cd₂V₂O₇ as the photocatalyst at room temperature and normal atmospheric pressure. CdV₂O₆ or Cd₂V₂O₇ (50 mg) and an MB aqueous solution (100 mL, 1 × 10⁻⁵ M) were added to the reactor. The mixture was stirred with a magnetic stirrer prior to irradiation with a xenon lamp at room temperature. Prior to irradiation, the solution was kept in the dark for 60 min to ensure the equilibrium of the working solution. After the reaction, the sample solution was put in a centrifuge to remove CdV₂O₆ or Cd₂V₂O₇ from the solution. The solution obtained this way was extracted into a quartz cell. The absorbance of the samples was measured with quartz cells every 60 min.

Calculation Approach: The hydrolysis constant of NH₄Cl (Kₐ) can be calculated from following formula: Kₐ = Kᵣ/Kₛ, where Kᵣ is the ion product constant of water and Kₛ is the equilibrium dissociation constant of ammonia.

Supporting Information (see footnote on the first page of this article): C/(C₀-time plots of the photocatalytic degradation of MB and MB solution with CdV₂O₆ in the dark.

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