Promotion of the Photocatalytic Activity of $\text{H}_4\text{Nb}_6\text{O}_{17}$ by Modifying the Layered Structure

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The layered structure of $\text{H}_4\text{Nb}_6\text{O}_{17}$ prepared by the proton exchange of $\text{K}_4\text{Nb}_6\text{O}_{17}$ was modified by using various *n*-alkylamines as swelling agents to enlarge the interlayer space. The incorporation of TiO_2 into the interlayer space was also attempted. XRD, EDX, and TG-DTA measurements were employed to characterize the products. The photocatalytic activities were evaluated by NO_x destruction under photo-irradiation with different light wavelengths. The results showed that the photocatalytic activity of a layered compound could be significantly promoted just by enlarging the interlayer space of it. And the incorporation of TiO_2 could further enhance the activity.

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1. Introduction

Due to the unique, highly applicable chemical and physical properties, layered compounds have been widely studied in the past decades. Layered compounds have potential applications in various fields such as energy-storage, electrocatalysis, novel energy-conversion systems, etc.^(1),2) Among them, the applications in photocatalysis also attract much attention; in particular, interest is in the photocatalytic performance of a layered compound intercalated metal oxides or organic molecules into the interlayer region. It is reported that by incorporating metal oxides or organic molecules the electric, magnetic, optical or catalytic properties of the layered compounds can be improved.^(3),4) Yamanaka et al.,⁽⁵⁾ Enena and Bard,⁽⁶⁾ Yoneyama et al.,^(7)–9) and Sato et al.^(10)–12) have reported the incorporation of extremely small particles of Fe_2O_3 , TiO_2 , CdS and CdS–ZnS mixtures, less than 1 nm in thickness, into the interlayer of layered compounds, such as montmorillonite, layered double hydroxides, layered niobate and layered titanate. As expected, the photocatalytic activities of the incorporated semiconductors were much higher than those of unsupported semiconductors; such enhancements in the photocatalytic activities were mainly attributed to the effective charge separation by the coupling of two semiconductors. While in this paper, we successfully promoted the photocatalytic activity of a layered compound $\text{H}_4\text{Nb}_6\text{O}_{17}$ only by enlarging the interlayer space without coupling it with a second semiconductor. It was suspected that the modified structure with a larger interlayer space could provide not only easy accessibility of guest molecules to active sites but also more chances to receive both light and guest molecules. The photocatalytic activity could be further enhanced by the incorporation of TiO_2 into the interlayer space.

2. Materials and methods

Synthesis

A layered compound $\text{K}_4\text{Nb}_6\text{O}_{17}$ was prepared by calcining a stoichiometry mixture of Nb_2O_5 and K_2CO_3 at 1473 K for 20 min in a platinum crucible.⁽¹³⁾ A total of 5 g $\text{K}_4\text{Nb}_6\text{O}_{17}$ was stirred in 250 cm³ of a 5 M HCl solution for 5 h at 60°C to realize ion exchange between K^+ and H^+ . The ion-exchanged product was separated by filtration, rinsed with distilled water and then dried in vacuum at 60°C overnight. Next, 2 g of the

acid-exchanged solid was dispersed in 400 cm³ of a 50 vol.% $\text{C}_n\text{H}_{2n+1}\text{NH}_2$ ($n=3,8$) solution and with vigorously stirring the mixture was refluxed for 2–3 d to intercalate *n*-alkylamine. After that, the prepared solid was stirred in a clear solution of $[\text{Ti}(\text{OH})_x(\text{CH}_3\text{CO}_2)_y]^{z+}$ for 120 h at room temperature, where $[\text{Ti}(\text{OH})_x(\text{CH}_3\text{CO}_2)_y]^{z+}$ was prepared by Kao and Yang's method,⁽¹⁴⁾ starting with $(i\text{-C}_3\text{H}_7\text{O})_4\text{Ti}$, CH_3COOH and H_2O in a 1 : 16 : 20 volume ratio. Finally, the obtained sample, after being filtered off and rinsed with water, was dispersed in water, and irradiated with UV light of a 450 W high-pressure mercury lamp at room temperature for 12 h to decompose the organics in the product.

Analysis

The crystalline phases of the products were identified by X-ray diffraction analysis (XRD, Shimadzu XD-D1) using graphite-monochromized $\text{CuK}\alpha$ radiation. The chemical compositions of the products were determined by EDX spectrometer (Rayny EDX-800HS, Shimadzu). The specific surface areas of the samples were measured by a surface area & pore size analyzer (Quantachrome Instruments, NOVA 4200e). The absorption edges of the products were determined from the onsets of diffuse reflectance spectra of the samples measured using an UV-vis spectrophotometer (Shimadzu UV-2450).

Photocatalytic reactions

The photocatalytic activity for nitrogen monoxide destruction was determined by measuring the concentration of NO gas at the outlet of the reactor during the photo-irradiation of a constant flow of a mixture containing 1 ppm NO --- 50 vol.% air (balance N_2).⁽¹⁵⁾ The photocatalytic sample was placed in a hollow of 20 mm length $\times$ 16 mm width $\times$ 0.5 mm depth of a glass holder plate and set in the bottle center of the reactor. A 450 W high-pressure mercury arc was used as the light source. The wavelength was controlled by selecting filters, i.e., Pyrex glass for >290 nm, Kenko L41 Super Pro (W) filter >400 nm and Fuji triacetyl cellulose filter >510 nm. The concentration of NO was determined using a NO_x analyzer (Yanaco, ECL-88A).

3. Results and discussion

The results of EDX measurements were summarized in Table 1. The detected chemical compositions of prepared $\text{K}_4\text{Nb}_6\text{O}_{17}$ were quite close to the calculated values. The results revealed that about 70 mol% K^+ was replaced by H^+ after proton exchange, and $\text{H}_4\text{Nb}_6\text{O}_{17}/\text{TiO}_2$ contained about

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Table 1. Chemical Components and Specific Surface Area of the Samples

Sample	Content		S.S.A. / m ² g ⁻¹
	K/Nb (molar ratio)	TiO ₂ / mass%	
K ₄ Nb ₆ O ₁₇	0.62	0	1.3
H ₄ Nb ₆ O ₁₇	0.19	0	6.2
H ₄ Nb ₆ O ₁₇ /n-C ₃ H ₇ NH ₂	0.13	0	2.5
H ₄ Nb ₆ O ₁₇ /n-C ₈ H ₁₇ NH ₂	0.21	0	3.9
H ₄ Nb ₆ O ₁₇ /TiO ₂	0.07	5	14.7

Fig. 1. XRD patterns of K₄Nb₆O₁₇ (a), H₄Nb₆O₁₇ (b), H₄Nb₆O₁₇/n-C₃H₇NH₂ (c), H₄Nb₆O₁₇/n-C₈H₁₇NH₂ (d) and H₄Nb₆O₁₇/TiO₂ (e).

5 mass% of TiO₂.

Table 1 also shows the specific surface areas (S.S.A.) of the samples determined by BET measurements. It is observed that the S.S.A. increased after proton exchange, probably due to proceeding certain degrees of exfoliation under acid treatment. The S.S.A. slightly decreased by the intercalation with n-alkylamines, indicating that the interlayer space was occupied by organic molecules. When the organics were decomposed after intercalating TiO₂ by UV light irradiation, the S.S.A. increased and was even larger than that of H₄Nb₆O₁₇ before intercalating alkylamines.

Figure 1 depicts the X-ray powder diffraction patterns of (a) K₄Nb₆O₁₇, (b) H₄Nb₆O₁₇, (c) H₄Nb₆O₁₇/n-C₃H₇NH₂, (d) H₄Nb₆O₁₇/n-C₈H₁₇NH₂ and (e) H₄Nb₆O₁₇/TiO₂. K₄Nb₆O₁₇ showed almost a single orthorhombic crystal phase (PDF 76-0977) with the interlayer distance of 0.82 nm. The protonated compound, H₄Nb₆O₁₇, still retained the structure of the parent compound except for a very slight shift of the 040 diffraction peak to the higher 2 theta angle, which was attributed to the slightly decrease of the interlayer distance by the substitution of K⁺ into H⁺. On the XRD patterns of sample (c) and (d), diffraction peaks at low 2 theta angle regions were observed, which was typical for the compound with large interlayer distance. Compared the XRD patterns of sample (c) and (d) with that of sample (b), significant shifts of diffraction peaks to lower 2 theta angle were observed, indicating the expansion of the interlayer by the intercalation

Fig. 2. TG-DTA analysis of H₄Nb₆O₁₇ (a), H₄Nb₆O₁₇/n-C₃H₇NH₂ (b), H₄Nb₆O₁₇/n-C₈H₁₇NH₂ (c) and H₄Nb₆O₁₇/TiO₂ (d).

of alkylamine. Since the length of octylamine molecule is greater than propylamine, the interlayer distance of sample (d), 2.36 nm, was also greater than that of sample (c), 1.61 nm. Since the sample (e) was irradiated by UV light to decompose the organics, the interlayer distance decreased to 0.91 nm, but was still greater than that of sample (b), 0.80 nm, due to the incorporation of TiO₂ particles.

Typical thermogravimetry-differential thermal analysis (TG-DTA) curves of the samples are shown in **Fig. 2**. The weight loss of sample (a) was due to the dehydration of H₄Nb₆O₁₇ to form Nb₂O₅, while those of samples (b) and (c) were due to the dehydration and oxidative decomposition of alkylamine molecules intercalated in the interlayer space. Therefore, H₄Nb₆O₁₇ intercalated with alkylamine showed a larger weight loss than the untreated H₄Nb₆O₁₇. H₄Nb₆O₁₇ intercalated with octylamine showed a larger weight loss than that with propylamine due to the larger molecular mass of octylamine. The weight loss of the sample (d), which was prepared by irradiating UV light after incorporating TiO₂ in sample (c), was significantly smaller than that of the sample (c), but still larger than that of untreated H₄Nb₆O₁₇ (sample (a)). It may be attributed to some residual organics. On the DTA curves of the samples, the dot lines shown in **Fig. 2**, the sharp exothermic peaks observed for samples (b) and (c) were mainly due to the oxidative decomposition of alkylamines. Since sample (c) was actually the precursor of sample (d), both of them showed exothermic peaks at the similar temperature range, around 360°C. Compared with that of sample (c), the intensity of the exothermic peak of sample (d) around 360°C was much lower, indicating the decrease in the amount of alkylamine in sample (d).

The UV-Vis diffuse reflectance spectra of (a) H₄Nb₆O₁₇, (b) H₄Nb₆O₁₇/n-C₈H₁₇NH₂ and (c) H₄Nb₆O₁₇/TiO₂ are shown in **Fig. 3**. By comparing the data of samples (a) and (b), it was observed that the absorption edge of H₄Nb₆O₁₇ did not change so much after intercalation with octylamine, and the calculated band gap energies of H₄Nb₆O₁₇ and H₄Nb₆O₁₇/n-C₈H₁₇NH₂ were 3.4 and 3.3 eV, respectively. Sample (c) was brown and showed absorption of visible light from 400 nm to 700 nm, since organics were not completely decomposed by UV irradiation, as we know usually brown color of the samples is caused by the existence of residual carbon which

Fig. 3. Diffuse reflectance spectra of $\text{H}_4\text{Nb}_6\text{O}_{17}$ (a), $\text{H}_4\text{Nb}_6\text{O}_{17}/n\text{-C}_8\text{H}_{17}\text{NH}_2$ (b) and $\text{H}_4\text{Nb}_6\text{O}_{17}/\text{TiO}_2$ (c).

Fig. 4. DeNO_x ability of $\text{H}_4\text{Nb}_6\text{O}_{17}$ (a), $\text{H}_4\text{Nb}_6\text{O}_{17}/n\text{-C}_3\text{H}_7\text{NH}_2$ (b), $\text{H}_4\text{Nb}_6\text{O}_{17}/n\text{-C}_8\text{H}_{17}\text{NH}_2$ (c) and $\text{H}_4\text{Nb}_6\text{O}_{17}/\text{TiO}_2$ (d).

related to the partly decomposed organics.

Figure 4 shows the photocatalytic activity of the powders under irradiation of light with various wavelength ranges. It can be seen that all samples showed low activity in visible light region, which may be attributed to the large band gap energy of the samples. For the sample (d), which contained about 5 mass% TiO_2 , showed a little higher activity than other three ones under the light with the wavelength > 400 nm, due to the relatively low band gap energy of TiO_2 . In the ultra violet (UV) light region, it is obvious that the activity of $\text{H}_4\text{Nb}_6\text{O}_{17}$ was significant promoted by the intercalation of alkylamine, and the incorporation of TiO_2 could further promote the activity. It was considered that the incorporation of alkyla-

mine led to the swelling of the interlayer space of layered compound, thus, NO_x molecules could get into the interlayer space more easily, which favored the photocatalytic reaction taking place in it. After the incorporation of TiO_2 and the decomposition of the organics, the specific surface area of the sample was significantly increased, i.e., two times larger than that of untreated $\text{H}_4\text{Nb}_6\text{O}_{17}$. This also favored the photocatalytic reaction and led to the further promotion of activity. On the other hand, the incorporation of TiO_2 might decrease the density of photo-induced electrons on $\text{H}_4\text{Nb}_6\text{O}_{17}$ by the heterogeneous charge transfer from $\text{H}_4\text{Nb}_6\text{O}_{17}$ to TiO_2 to depress the recombination of electrons and holes, which would also promote the activity of the sample.

4. Conclusions

The interlayer space of layered compound $\text{H}_4\text{Nb}_6\text{O}_{17}$ was successfully swelled by the intercalation of alkylamine, and by reacting $\text{H}_4\text{Nb}_6\text{O}_{17}/n\text{-C}_8\text{H}_{17}\text{NH}_2$ with a titanyl acylate complex solution, followed by the irradiation with UV-light, TiO_2 was also successfully incorporated into the enlarged interlayer space.

With expanding interlayer space, the photocatalytic activity (DeNO_x ability) of $\text{H}_4\text{Nb}_6\text{O}_{17}$ under UV light irradiation was significantly promoted, and was further promoted by incorporating TiO_2 into the enlarged interlayer space.

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