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On the enhanced catalytic activity of TiO_2-supported layered compounds for Cr(VI) photo-reduction

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Abstract

TiO_2 supported layered compounds (SLCs) with different loading amounts of layered compound (LC) were prepared via impregnating TiO_2 with a KOH solution and then calcining at high temperature. The photo-reduction of Cr(VI) catalyzed by SLCs and LC was also examined. Results showed that LCs were observed in the surface of SLCs and they were generated by a solid-phase reaction between KOH/K_2CO_3 and TiO_2 at high temperature. At a solution pH of 1.0, the Cr(VI) photo-reduction showed 1/2 order kinetics in the presence or absence of TiO_2. However, the Cr(VI) photo-reduction catalyzed by LC fitted zero order kinetics. In the presence of SLC with low loading amount of LC, the Cr(VI) photo-reduction showed the same kinetics as that over TiO_2. In contrast, the kinetics of Cr(VI) photo-reduction catalyzed by SLC with high loading amount of LC was similar to that by the unsupported LC. SLC with a certain loading amount of LC exhibited enhanced catalytic activity for Cr(VI) photo-reduction. The enhanced catalytic activity was related to the electron transfer between the support and the LC.

Keywords: Layered compound; Support; Cr(VI) photo-reduction; Catalysis; Kinetics

1. Introduction

From the viewpoint of energy conversion from solar energy, special attention has been paid to catalytic photochemical processes recently [1–3]. As one of the advanced oxidation processes, pollutant treatments by photochemical techniques have been also studied extensively [4–8]. Typical semiconductors, such as TiO_2, ZnO, CdS, ZnS, etc. are usually adopted as effective catalysts in catalytic photochemical procedures, such as metal recovery, gaseous pollutant removal and total mineralization of organic pollutants. Under the illumination of UV/visible light with energy equal to or larger than the band gap energy of semiconductor, electron–hole pairs (e^-–h^+) can be triggered to the conduction band and valance band of the semiconductor, respectively. Besides recombining to generate heat, electron and hole can also transfer to the surface of the semiconductor and then oxidize the acceptor substrate or reduce the donor substrate adsorbed in the surface of semiconductors [9].

Industrial effluents from electroplating processes, pigment and paint industries usually contain the very toxic heavy metal Cr(VI). A typical treatment of Cr(VI) is based on its reduction to less toxic Cr(III) by $NaHSO_3$ or $FeSO_4$ and then the precipitation of Cr(III) at a neutral or alkaline solution. The catalytic photo-reduction of Cr(VI) to Cr(III) has been proved to be a practical and clean alternative [10–12]. The catalytic materials usually used for Cr(VI) photo-reduction are metal oxides and metal sulfates, including ZnO, TiO_2, WO_3 and CdS, etc.

Recently, some novel layered compounds (LCs) have been found to be especially active in catalyzing water splitting to generate H_2 and O_2 under UV illumination [13–15]. The high catalytic efficiency is due to the effective separation of photo-generated electron–hole pair by the specific structure of LCs [16]. Therefore, a great diversity of LCs have been synthesized and modified to obtain efficient photo-catalysts for water splitting [17]. After the doping of superfine metal/metal oxides in the interlayer, LCs showed high catalytic efficiency in water splitting. Furthermore, the modification of LCs by the intercalation of a TiO_2 pillar into the layers also showed an enhanced catalytic effect in water splitting with the electron transfer between host and guest contributing to the increase in photo-catalytic efficiency [18–20]. Less attention, however, has been paid to the application of LCs as catalysts in the photochemical treatment of wastewater. Our previous results indicated that

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Cr(VI) photo-reduction catalyzed by layered titanate exhibited unique photo-catalytic kinetics which was different from those using typical inorganic oxide semiconductors, such as TiO_2 and ZnO [21]. In this study, we report the preparation of novel supported layered compounds (SLCs) and their enhanced catalytic activity for Cr(VI) photo-reduction.

2. Experimental

2.1. Preparation of catalysts

Commercial TiO_2 was obtained from the Shanghai TiO_2 plant and used as a support. The sample was calcined at 1073 K for 24 h prior to the impregnation and test of photo-catalytic. SLCs were prepared by impregnating TiO_2 with a solution of 0.1 M KOH. Impregnation was carried out at 363 K in a water bath for about 3 h until the water was evaporated. The resulting samples were dried at 383 K for 4 h. The products were calcined at 1073 K for 24 h, and the final product was referred to as $K_2Ti_6O_{13}/TiO_2$ (the loading amount of $K_2Ti_6O_{13}$). The loading amount was calculated based on the additional amount of KOH. The unsupported LC was hydro-thermally synthesized. Under vigorous stirring, a mixture of isopropanol and titanium tetraisopropoxide was added dropwise to a mixture of an aqueous solution of 1 M KOH and isopropanol (titanium tetraisopropoxide/KOH $= 1/2$, molar ratio). The gel generated was stirred at ambient temperature for 2 h. The mixture was transferred to an autoclave and maintained at 523 K for 1 week. The resulting mixture was filtered and repeatedly washed with distilled water. Finally, after the filtration cake was dried at 383 K for 4 h, it was calcined at 1073 K for 24 h.

2.2. Catalyst characterization

Ultra violet diffuse reflectance spectra (UV-DRS) of catalysts were collected using a Shamazu-UV-240. MgO powder was used as a reference. The scan range varied from 200 to 600 nm. X-ray powder diffraction (XRD) patterns of LCs and SLCs were obtained on a Japan XD-3AX diffractometer using Cu Kα radiation.

2.3. Catalytic Cr(VI) photo-reduction

Cr(VI) photo-reduction was carried out in a NDC reactor. A high pressure mercury lamp (500 W) was used as the UV light source and cooling water through a jacket around the lamp was used to remove the heat generated by the high pressure lamp during the illumination. The lamp was inserted into a well within a 500 ml cylindrical Pyrex vessel and the reaction solution could be irradiated directly by the UV light source without filtration. In a typical photo-catalytic run, 210 mg of catalyst was added to 300 ml of 140 ppm Cr(VI) solution. Its pH value was adjusted to 1.0 by using concentrated sulfuric acid prior to the photoreaction. The catalyst was suspended in the solution under stirring for 4 h to reach the adsorption equilibrium before the photo-reduction test. Aqueous samples were taken at regular intervals, suspended catalyst particles were removed by filtration, and the Cr(VI) concentration of these samples was determined spectra-photo-metrically.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 showed the XRD patterns of supported and unsupported LCs. After being calcined at 1073 K, the titanium dioxide used as a support contained both anatase and a small amount of rutile. The hydro-thermally synthesized sample showed poor crystallinity after being autoclaved at 523 K for 1 week and it could be considered as amorphous material. This implied that the LC was very difficult to crystallize at low temperature. After being calcined at 1073 K for 24 h, the sample obtained showed strong XRD peaks that could be attributed to layered $K_2Ti_6O_{13}$. For supported samples, XRD spectra showed that $K_2Ti_6O_{13}$ appeared in the surface of all samples synthesized by impregnation followed by calcination at high temperature. It was obvious that the LC was generated from the solid-phase reaction of KOH/K_2CO_3 with TiO_2 at high temperature. In comparison to the TiO_2 support, the obviously increased amount of rutile in SLC implied that the existence of KOH/K_2CO_3 enhanced the crystalline transfer of TiO_2 from anatase to rutile during the calcination at high temperature. As the loading amount of KOH increased, the intensity of XRD peak of $K_2Ti_6O_{13}$ increased, which indicated that the amount of $K_2Ti_6O_{13}$ in the surface of the supported sample increased.

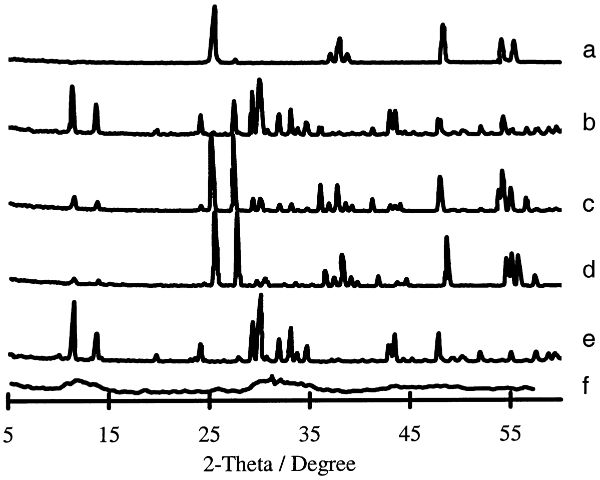

Fig. 1. XRD spectra of: (a) TiO_2; (b) $K_2Ti_6O_{13}/TiO_2$ (63%); (c) $K_2Ti_6O_{13}/TiO_2$ (37.9%); (d) $K_2Ti_6O_{13}/TiO_2$ (19.5%); (e) $K_2Ti_6O_{13}$ after calcination; (f) $K_2Ti_6O_{13}$ before calcination.

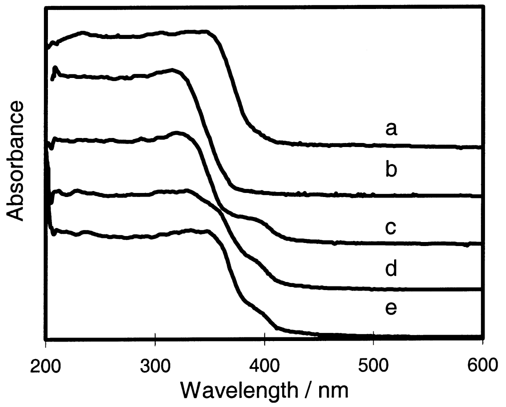

Fig. 2. The UV–VIS reflection spectra of: (a) TiO_2; (b) $K_2Ti_6O_{13}$; (c) $K_2Ti_6O_{13}/TiO_2$ (63%); (d) $K_2Ti_6O_{13}/TiO_2$ (37.9%); (e) $K_2Ti_6O_{13}/TiO_2$ (19.5%).

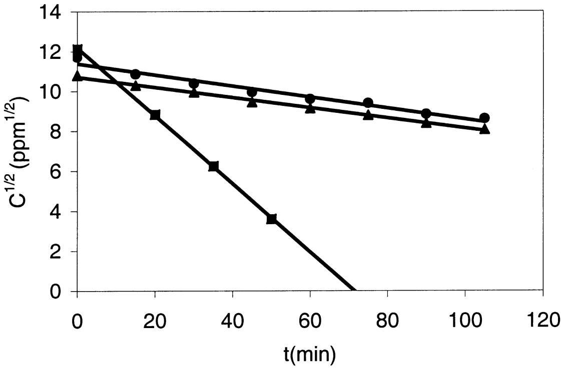

Fig. 3. Cr(VI) photo-reduction catalyzed by different catalysts: (▲), TiO_2; (●), $K_2Ti_6/O_{13}/TiO_2$ (19.5%); (■) $K_2Ti_6O_{13}/TiO_2$ (37.9%).

Comparing the XRD pattern of $K_2Ti_6O_{13}/TiO_2$ (19.5%) with that of $K_2Ti_6O_{13}/TiO_2$ (37.9%), we noticed that, with increase in KOH loading amount, the peak intensity of anatase decreased evidently and rutile increased slightly, and the amount of surface $K_2Ti_6O_{13}$ increased. As $K_2Ti_6O_{13}$ loading amount equal to 63.0%, surface anatase completely disappeared and rutile decreased thereafter.

The UV-DRS spectrum of calcined TiO_2 showed the typical UV absorbance of anatase (see Fig. 2). However, the UV absorbance of rutile was invisible due to the small amount of rutile in the support. Compared with UV absorbance of TiO_2, UV absorbance of $K_2Ti_6O_{13}$ showed a blue shift by about 30 nm. It indicated that the band gap energy of $K_2Ti_6O_{13}$ was larger than that of TiO_2. The UV-DRS patterns of SLCs showed that rutile exited in the surface of these materials and the increased UV absorbance of rutile indicated that the amount of rutile increased as the loading amount of LC increased. This was in agreement with XRD results. The main UV absorbance of SLC was gradually blue-shifted as the loading amount of LC increased. It was noteworthy that the absorbance of anatase and LCs were not differentiated in the UV-DRS patterns of SLCs. This possibly implied that there was an energy exchange or electron transfer between TiO_2 and LC in SLCs.

3.2. Kinetics of catalytic Cr(VI) photo-reduction

Under UV illumination, Cr(VI) was reduced to Cr(III) in the presence or absence of photo-catalysts. The overall reaction of Cr(VI) reduction could be described as follows.

$$2Cr_2O_7^{2-} + 16H^+ = 4Cr^{3+} + 8H_2O + 3O_2$$

At a pH of 1.0, the photo-reduction of Cr(VI) shows 1/2 order kinetics. However, its kinetics changes to first order at a pH of 4.0 or higher [22,23]. The photo-catalytic efficiency or the reaction rate of Cr(VI) photo-reduction is also dependent on the solution pH. A high efficiency of Cr(VI) photo-reduction is expected at low pH. The addition of catalyst, usually metal oxide semiconductors, does not change the kinetics of photo-reduction.

Fig. 3 showed that, at a pH of 1.0, Cr(VI) photo-reduction exhibited 1/2 order kinetics in the presence of TiO_2. It was already reported that the kinetics of Cr(VI) photo-reduction fitted 1/2 kinetics in the absence of catalyst [23]. Thus, the addition of TiO_2 did not lead to the change in the kinetics of Cr(VI) photo-reduction. Cr(VI) photo-reduction catalyzed by hydro-thermally synthesized $K_2Ti_6O_{13}$ displayed specific zero order kinetics (see Fig. 4), which was similar to our previous results of Cr(VI) photo-reduction catalyzed by other serial LCs, $K_2Ti_4O_9$, H^+ exchanged $K_2Ti_4O_9$ and $K_2Ti_8O_{17}$ [21]. The novel kinetics possibly implied that the mechanism of Cr(VI) photo-reduction catalyzed by LCs was different from that by typical semiconductors.

The kinetics of Cr(VI) photo-reduction catalyzed by $K_2Ti_6O_{13}/TiO_2$(37.5%) or $K_2Ti_6O_{13}/TiO_2$ (19.5%) was 1/2 order, the same kinetics as that by TiO_2, although XRD results showed a significant amount of $K_2Ti_6O_{13}$ in the surface of $K_2Ti_6O_{13}/TiO_2$ (37.5%) or $K_2Ti_6O_{13}/TiO_2$ (19.5%). In the presence of the SLC with the highest $K_2Ti_6O_{13}$ loading amount (63%) the catalytic photo-reduction of Cr(VI) also exhibited zero order kinetics, which was similar to that of hydro-thermally synthesized LC and our previous

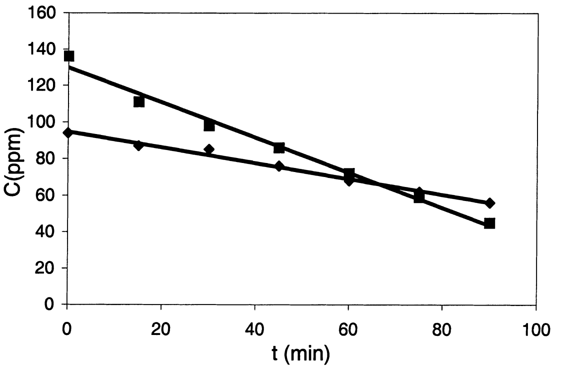

Fig. 4. The photo-catalytic removal of Cr(VI) in the presence of (■), $K_2Ti_6O_{13}/TiO_2$ (63.0%); (◆), $K_2Ti_6O_{13}$.

results. The XRD pattern of this material showed that there existed LC as well as rutile in the surface.

For SLC, the catalytic kinetics of Cr(VI) photo-reduction was dependent on the adsorption and catalytic ability of different surface species. LC and rutile had low specific surface area and surface hydroxide concentration. A low Cr(VI) adsorption capacity over LC and rutile could thus be expected. Comparatively, anatase had a higher adsorption capacity. For $K_2Ti_6O_{13}/TiO_2$ (37.5%) or $K_2Ti_6O_{13}/TiO_2$ (19.5%), Cr(VI) was possibly adsorbed preferentially on the anatase and the photo-reduction of Cr(VI) happened over the surface of TiO_2. It was also possible that the catalytic efficiency of Cr(VI) photo-reduction over layered species was negatively low because of the low Cr(VI) adsorption capacity on LC. Therefore, the catalytic Cr(VI) photo-reduction over these catalysts exhibited 1/2 order kinetics although a marked amount of LC appeared in the surface. For $K_2Ti_6O_{13}/TiO_2$ (63.0%), the photo-catalytic activity and Cr(VI) adsorption capacity of rutile was too low, as had been reported previously [23,24], to impose its catalytic influence on the Cr(VI) photo-catalytic kinetics. Therefore, although Cr(VI) photo-reduction catalyzed by rutile fitted 1/2 order kinetics, Cr(VI) photo-reduction catalyzed by $K_2Ti_6O_{13}/TiO_2$ (63%) showed zero order kinetics which was typical of the catalytic characteristics of LC.

3.3. *Catalytic activities of Cr(VI) photo-reduction*

The reaction rates of Cr(VI) photo-reduction by different catalysts were listed in Table 1. The catalytic efficiency of Cr(VI) photo-reduction increased in the presence of TiO_2. After calcination at high temperature, the catalytic activity of TiO_2 slightly decreased. This was possibly a decrease in surface area, the hydroxide concentration of TiO_2 surface and the change in crystalline form of TiO_2 caused by high temperature calcination.

The rate constant of Cr(VI) photo-reduction catalyzed by hydro-thermally synthesized $K_2Ti_6O_{13}$ was $1.38 \times 10^{-7}\,M\,s^{-1}$ which was lower than that of $K_2Ti_6O_{13}/TiO_2$ (63%) ($3.07 \times 10^{-7}\,M\,s^{-1}$). It appeared that the catalytic activity of SLCs with high loading amount of LC was higher than that of unsupported LC. This was due to the effective dispersion of layered $K_2Ti_6O_{13}$ over the support that led to the enhancement of photo-catalytic activity of SLC.

Table 1
Rate constants of Cr(VI) photo-reduction catalyzed by different catalysts

Catalysts	Kinetics	Rate constants	Units
Catalyst free	1/2	1.65×10^{-6}	$M^{1/2}\,s^{-1}$
TiO_2 (before calcination)	1/2	2.04×10^{-6}	$M^{1/2}\,s^{-1}$
TiO_2 (after calcination)	1/2	1.88×10^{-6}	$M^{1/2}\,s^{-1}$
$K_2Ti_6O_{13}/TiO_2$ (19.5%)	1/2	2.05×10^{-6}	$M^{1/2}\,s^{-1}$
$K_2Ti_6O_{13}/TiO_2$ (37.9%)	1/2	1.25×10^{-5}	$M^{1/2}\,s^{-1}$
$K_2Ti_6O_{13}/TiO_2$ (63%)	0	3.07×10^{-7}	$M\,s^{-1}$
$K_2Ti_6O_{13}$	0	1.38×10^{-7}	$M\,s^{-1}$

Compared with TiO_2, $K_2Ti_6O_{13}$ (19.5%) showed slightly enhanced catalytic activity for Cr(VI) photo-reduction. Furthermore, the photo-catalytic activity of $K_2Ti_6O_{13}/TiO_2$ (37.9%) for Cr(VI) photo-reduction was dramatically accelerated compared with the hydro-thermally synthesized LC or other SLCs.

For $K_2Ti_6O_{13}$ (19.5%) and $K_2Ti_6O_{13}$ (37.9%), the reaction kinetics suggested the Cr(VI) photo-reduction possibly occurred at the surface of TiO_2. However, the catalytic active sites were reduced as expected because the amount of TiO_2 was reduced after solid-state reaction between KOH/K_2CO_3 and TiO_2. XRD patterns revealed that there were three species in the surface: rutile, anatase and LC. It was deduced that the influence of rutile on the enhancement of the photo-catalytic activity could be excluded as no significant enhancement of catalytic activity was observed in the presence of SLC with 63% loading amount of LC, in which there were only LC and rutile in the surface. Therefore, the enhanced catalytic activity could be attributed to the interaction between LC and anatase.

Uchida et al. [25] and Sato et al. [26] studied TiO_2 pillared LCs and found an interaction between the TiO_2 pillar and LC. They suggested a charge injection process between guest and host after UV illumination. The key point of this process was the injection of an electron from the conduction band of TiO_2 to the conduction band of LC. In our study, therefore, an estimation of band gap energy and band edge potential of LC would be helpful to understand the interaction between TiO_2 and LC.

Based on the UV-DRS absorbance of the LC, its band gap was estimated to be 3.50 eV blue-shifted by about 0.28 eV with respect to TiO_2 (band gap energy: 3.22 eV). The band edge potential of LC, which was a type of semiconductor, could be obtained as follows [27,28].

$$E^0_{cs} = E^e - X + \tfrac{1}{2}E_g$$

where E^e, X, E_g denoted the energy of free electrons on the hydrogen scale (~4.5 eV), the electro-negativity of the semi-conductor, and the band gap energy of the semiconductor, respectively. The potentials of the conduction band of $K_2Ti_6O_{13}$ and anatase were predicted to be about −1.0 and 0.3, respectively. The scheme of electron transfer was thus showed in Fig. 5.

For the SLC, Cr(VI) was preferentially adsorbed in the surface of anatase. The excited electron in the conduction band of LC transferred to the conduction band of anatase and Cr(VI) adsorbed in the surface of anatase was reduced by excited electrons. Simultaneously, the enrichment of electrons in the conduction band of anatase led to the enhanced catalytic activity for Cr(VI) photo-reduction.

SLCs with different loading amounts showed different catalytic activity and kinetics for Cr(VI) photo-reduction. Therefore, it suggested that the distribution of LC and anatase in the surface played an important role in the catalytic activity and there was an optimal LC/anatase ratio

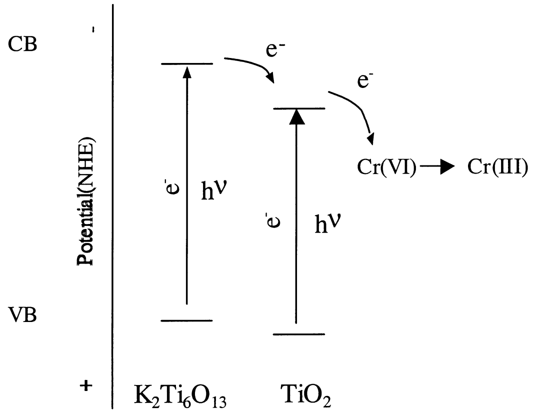

Fig. 5. Diagram of electron transfer between LC and TiO_2.

in the surface for the effective enhancement of Cr(VI) photo-reduction.

4. Conclusions

The photo-reduction of Cr(VI) at a pH of 1.0 showed 1/2 order kinetics in the presence of TiO_2 or absence of catalysts. However, the kinetics of Cr(VI) photo-reduction changed into zero order with LC as catalyst. At high loading amount of LC, SLC showed the same catalytic kinetics for Cr(VI) reduction as unsupported LC. However, its catalytic capability was about two times as high as that of unsupported LC. For SLC with low loading amount, the kinetics of Cr(VI) photo-reduction was 1/2 order although there was a significant amount of LC in the surface. The enhanced catalytic activity of $K_2Ti_6O_{13}/TiO_2$ (37.9%) was due to the electron transfer from the conduction band of LC to the conduction band of TiO_2 during the UV illumination.

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