Cr(VI) photoreduction catalysed by ion-exchangeable layered compounds

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Abstract

Layered compounds, $K_2Ti_4O_9$ and H^+ exchanged $K_2Ti_4O_9$, were prepared and Cr(VI) photoreductions catalysed by these layered compounds were carried out. Results showed that the acid strength and acid amount of layered compounds were increased with layered compound acid exchanged, but decreased with acid exchanged layered compound treated at 623 K. Adsorption capacity of layered compound for Cr(VI) increased after acid exchanging, while heating at high temperature led to a low adsorption capacity of layered compound. Cr(VI) photoreduction catalysed by $K_2Ti_4O_9$, $H^+– K_2Ti_4O_9$ or $H^+–K_2Ti_8O_{17}$ showed that the kinetic model, which fitted zero order, was different from that Cr(VI) photoreduction catalysed by typical semiconductors. The efficiency of Cr(VI) photoreduction catalysed by layered compounds, specially at the high solution pH value, was enforced by acid exchanging and the pre-treatment by heating. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cr(VI) photoreduction; Layered compounds; Ion-exchangeable

1. Introduction

Photocatalytic processes have received intensive attention from the viewpoint of solar energy utilisation [1–7]. Based on the potential application in environmental protection, pollutant treatments via Photochemical techniques have been studied extensively [8,9]. Most pollutants, organic or inorganic pollutants, can be removed effectively by using photochemical techniques [10,11]. Under most circumstances, catalyst addition can enhance the efficiency of pollutant photoremoval. Typical semiconductors, such as TiO_2, Fe_2O_3, ZnO, CdS etc., are usually adopted as effective catalysts in the photocatalytic procedures [12–14].

As novel photocatalytic as well as structured materials, some ion-exchangeable layered compounds have been studied in recent years. Studies on photocatalytic behaviours of layered compounds focus on the decomposition of water to generate H_2 and O_2 and it has been observed that some layered compounds have fairly high catalytic activity in the H_2O cleavage comparing with some typical semiconductors [15–19]. It seems the recombination of electron and hole triggered by band gap excitation can be hindered effectively with O_2 and H_2 generated in different interlayer spaces of layered compounds loaded with elemental nickel and high quantum efficiency can thereby be obtained.

Industrial effluents, coming from electroplating processes, pigment and paint industry contain heavy metal Cr(VI) which is very toxic. A typical treatment of Cr(VI) is based on its reduction to Cr(III) by $NaHSO_3$ or $FeSO_4$ and then precipitated. Cr(VI) photoreduction to Cr(III) catalysed by semiconductors, such as TiO_2, ZnO, WO_3, and CdS, is studied as an available alternative [20–22].

In this paper, layered compounds, $K_2Ti_4O_9$ and H^+ exchanged $K_2Ti_4O_9$, were prepared and used to catalyse Cr(VI) photoreduction. Meanwhile, the comparison of photocatalytic behaviours of layered compounds with that of TiO_2, a typical semiconductor, was also presented.

2. Experimental details

2.1. Preparation

(1) Layered compounds: $K_2Ti_4O_9$ was prepared by calcining the mixture of TiO_2 and anhydrous potassium carbonate (Ti/K=1.75 mole rate) at 1073 K for 24 h and then

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for another 24 h at 1073 K after grinding. H^+–$K_2Ti_4O_9$ was prepared by suspending 15 g $K_2Ti_4O_9$ in 300 ml 1 mol/l HCl aqueous solution and exchanging at 343 K for 6 h. H^+–$K_2Ti_4O_9$ was washed repeatedly by distilled water. Resultant product was dried at 423 K for 2 h. Then, partial dried product was calcined at 623 K for 2 h.

(2) TiO_2: With vigorous stirring at room temperature, a mixture of isopropanol and titanium tetraisopropoxide was added dropwise to the mixture of distilled water and isopropanol (H_2O/titanium tetraisopropoxide=1.5 volume rate), the mixture was filtered and gel washed by distilled water repeatedly to remove isopropanol. The resultant gel was dried at 383 K for 2 h and then calcined at 623 K for 4 h.

X-ray powder diffraction patterns of layered compounds were obtained on Japan XD-3AX diffractometer using CuK_α radiation.

Acidity of layered compounds was measured by microcalorimeter. In a typical run, 0.5 g sample was installed in a stable oven at 423 K and outgassed overnight. Calorimeter was maintained at 373 K, dosed NH_3 was introduced into the sample and the adsorption heat was recorded till the equilibrium pressure equalled 4 Tor.

The adsorption capacity of layered compounds for Cr(VI) was examined by static adsorption equilibrium. 0.5 g layered compound was suspended in 50 ml 50 ppm $K_2Cr_2O_7$ solution and the static adsorption process was allowed to continue for 24 h with stirring to reach the adsorption equilibrium then the catalyst was filtered and the Cr(VI) concentration was determined spectra-photometrically by using diphenylcarbazide as colour former.

Cr(VI) photoreduction was carried out at two different solution pH values in NDC reactor which was equipped with a 500 ml thermostatted cylindrical Pyrex vessel irradiated directly by the UV light source, a high pressure mercury lamp (500 W). Catalyst was suspended in the aqueous solution for 12 h in stirring to reach the adsorption equilibrium before the photoreaction. Cr(VI) concentration was about 40 ppm and the catalyst addition amount was 70 mg per 100 ml solution. Cr(VI) concentration of $K_2Cr_2O_7$ aqueous solution was determined in the same way as the adsorption examination.

3. Results and discussion

The structures of $K_2Ti_4O_9$, H^+–$K_2Ti_4O_9$ dried at 423 K, referred to as H^+–$K_2Ti_4O_9$ (423), and H^+–$K_2Ti_4O_9$ heated at 623 K, were determined by XRD and were in agreements with the results already reported [23–25]. H^+–$K_2Ti_4O_9$ (623) was changed into H^+–$K_2Ti_8O_{17}$ after further heating treatment at 623 K. It was observed that the dehydration as well as the condensation of layer occurred while heating at 623 and new layer constructed.

Concerning the adsorption capacity, different layered compounds show different adsorption capacities for Cr(VI).

Adsorption result shows the slight increase in the Cr(VI) adsorption capacity owing to the hydration of layer as well as the enlargement of interlayer space after acid exchanging [24]. Hydration of layer, which facilitates Cr(VI) diffusion into the interlayer of layered compounds, plays an important role in the exchanging and photohydrolysis of layered compounds. While, a little low Cr(VI) adsorption capacity is incurred by further heating of H^+–$K_2Ti_4O_9$ (423 K). After dehydration as well as condensation of layer at 623 K, H^+–$K_2Ti_8O_{17}$ attains a more rigid structure than H^+–$K_2Ti_4O_9$ (423 K). Dehydration of H^+–$K_2Ti_8O_{17}$ from H^+–$K_2Ti_4O_9$ (423 K) calcined at 623 K leads also to the loss of its interlayer space as well because of the condensation of layers, which is responsible for the lower Cr(VI) adsorption capacity than precuor layered compound $K_2Ti_4O_9$, without acid exchanging.

Differential heats of adsorption of NH_3 on layered compounds are showed in Fig. 1 as a function of NH_3 surface coverage. The initial differential heat value of 160 KJ/mol shows that there is strong acidic site in the interlayer of H^+–$K_2Ti_4O_9$ (423 K). The two evidently stepped decreases of differential heat indicate that there are homogeneous strong and mid-strong acidic sites in the interlayer of H^+–$K_2Ti_4O_9$ (423 K). The succeeding adsorption of NH_3 on the mid-strong and weak acidic sites of H^+–$K_2Ti_4O_9$ (423 K) indicates that there exist heterogeneous mid-strong and weak acidic sites. In contrast, the initial differential heat value of H^+–$K_2Ti_8O_{17}$, 30 KJ/mol, is far lower than that of H^+–$K_2Ti_4O_9$ (423 K), which implies that there is only weak acidic site in the interlayer of H^+–$K_2Ti_8O_{17}$ instead of strong and mid-strong acidic sites. Concerning the acidity amount, it can also be observed that the amount of acidic site of $K_2Ti_4O_9$ (423 K) is larger than that of H^+–$K_2Ti_8O_{17}$. The acidity of H^+ exchanged $K_2Ti_4O_9$ is similar with the acidity of $HLaNb_2O_7$, which reported by T. Matsuda [26,27]

In the presence and absence of a typical semiconductor, TiO_2, it is observed that the Cr(VI) photoreductions show different removal efficiencies at different solution pH
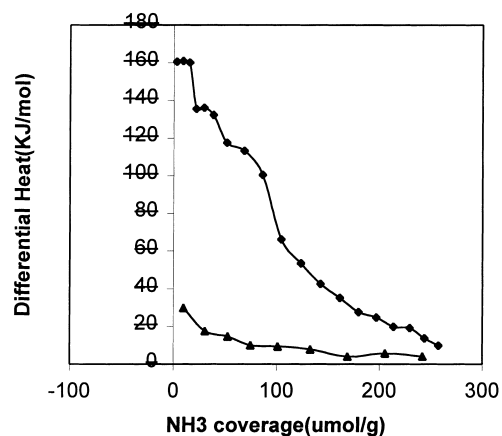

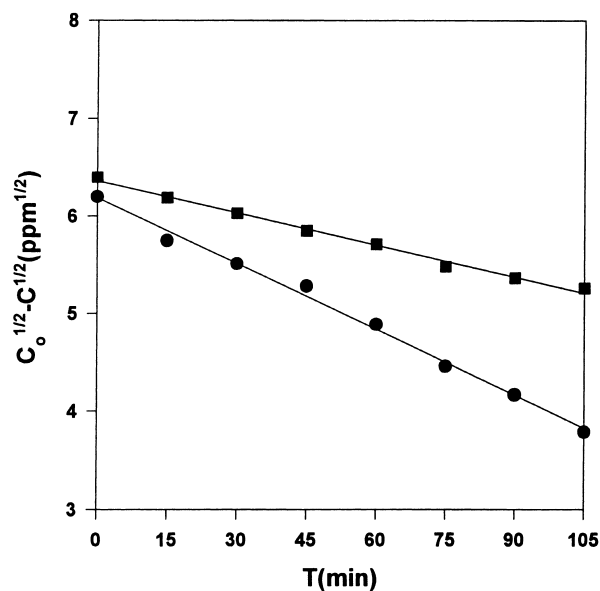Fig. 1. Differential heats of adsorption of NH_3 as a function of surface of coverage ◆: H^+–$K_2Ti_4O_9$ (423 K) ▲: H^+–$K_2Ti_8O_{17}$.

Fig. 2. The Cr(VI) photoreduction kinetics at different solution pH values in the absence of catalysts ■: pH 2.0 ●: pH 1.0.

the presence or absence of TiO_2 follow Eqs. (1) and (2):

$$-dC/dt = kC^{1/2} \qquad (1)$$

or

$$C_0^{1/2} - C^{1/21} = kt \qquad (2)$$

where k is the rate constant.

Cr(VI) photoreductions exhibit 1/2-order reaction kinetics. The kinetic results also agree with Aguado's and Yaneyama's results [28,29].

High photoreduction efficiency can be obtained at low solution pH value because the potential of CrO_4^{2-}/Cr^{3+} pair shifts to anode value with solution pH value increasing (98 mV per unit) [12].

In the presence of layered compounds, $K_2Ti_4O_9$, $H^+-K_2Ti_4O_9$ or $H^+-K_2Ti_8O_{17}$, the kinetics of Cr(VI) photoreduction at pH value of 1.0 or 2.0 is changed compared to the reduction of Cr(VI) in the presence or absence of TiO_2, it follows Eqs. (7) and (8):

$$-dC/dt = k \qquad (7)$$

or

$$C_0 - C = kt \qquad (8)$$

It is indicated that the kinetics of Cr(VI) photoreduction fits zero-order reaction kinetics in the presence of layered compounds at pH values of 1.0 or 2.0 Figs. 4 and 5.

In the presence of typical semiconductors, such as TiO_2, ZnO etc., Cr(VI) photoreductions show same kinetics as that in the absence of catalysts. The finding that the kinetics of Cr(VI) photoreduction is changed with layered compounds

values, while the kinetics of Cr(VI) photoremoval remains unchanged irrespectively of whether catalyst is present or absent. Detailed results of Cr(VI) photoreduction catalysed by different TiO_2 will be published elsewhere. Figs. 1 and 2 show the kinetics and catalytic efficiency of Cr(VI) photoreduction in the absence and presence of TiO_2 at different solution pH values.

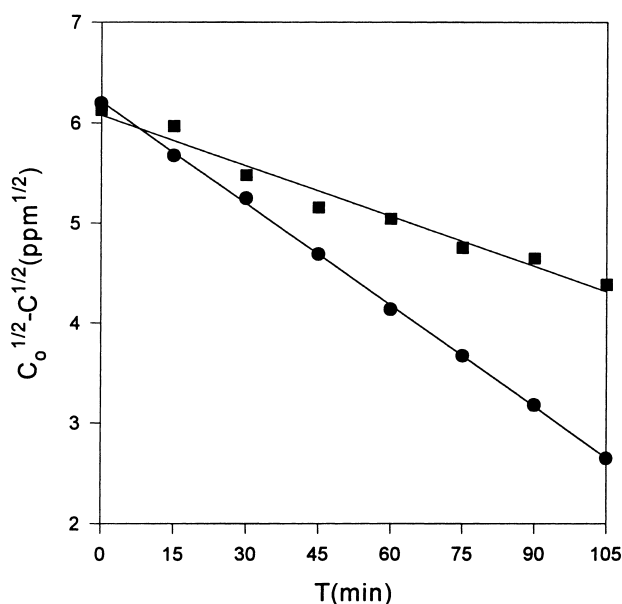As pH equals to 1.0 and 2.0, it is found by regression simulation that Cr(VI) photoreduction reactions Fig. 3 in

Fig. 3. The Cr(VI) photoreduction kinetics at different solution pH values in the absence of TiO_2 ■: pH 2.0 ●: Ph 1.0.

Fig. 4. The Cr(VI)(Fi) photoreduction kinetics at pH 1.0 in the presence of layered compounds ●: $K_2Ti_4O_9$ ▲: $H^+ - K_2Ti_4O_9$ ■: $H^+ - K_2Ti_8O_{17}$.
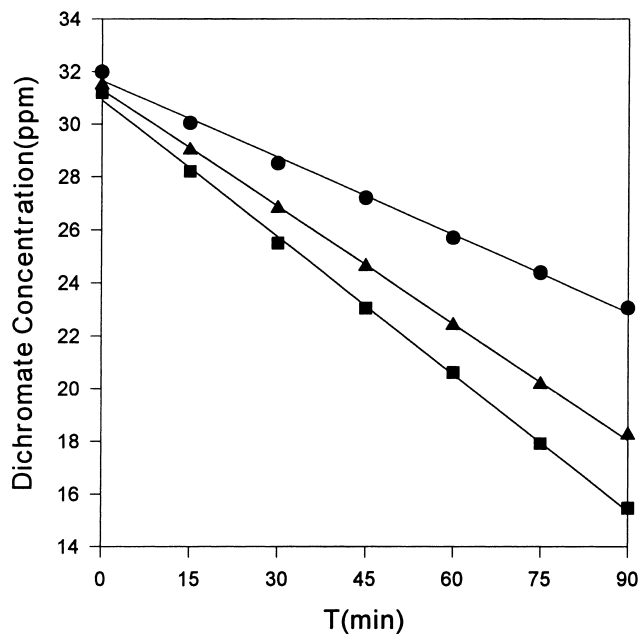
Fig. 5. Cr(VI) photoreduction kinetics at pH 2.0 in the presence of layered compounds ●: $K_2Ti_4O_9$ ▲: $H^+ - K_2Ti_4O_9$ ■: $H^+ - K_2Ti_8O_{17}$.

addition suggests that there is a particulate reduction mechanism in the Cr(VI) photoreduction catalysed by layered compounds which is different from that by typical semiconductors. Some specific photoreaction phenomena also were observed in the H_2O decomposition into H_2 and O_2 catalysed by some layered compounds [27].

The evident difference between TiO_2 and layered compounds is that the layered compound is a structured n-type semiconductor with two-dimensional structure, while TiO_2 is a nonporous material. The photoreduction procedure catalysed by layered compounds is more complicated than that catalysed by TiO_2 because the photoreduction of Cr(VI) happens in the interlayer of layered compounds while in the surface of TiO_2. It is important but difficult to determine the

rate-determining step for Cr(VI) photoreduction catalysed by layered compounds.

It is noteworthy that the particulate exchanging property play an important role in the photocatalytic ability. It is observed that $H^+ - K_2Ti_4O_9$ have constant K^+ exchanging capacity which is independent on the K^+ concentration in the bulk solution [30,31]. It may be proposed that the available adsorption and reduction site for Cr(VI) is limited and kept constant throughout the photoreduction procedure. It also can be proposed that photoreduction of adsorbed Cr(VI) in the interlayer, which is independent on the bulk Cr(VI) concentration, is the rate-determining step for photoreduction of Cr(VI) catalysed by layered compounds. Table 1

The results listed in Table 2 show that different layered compounds exhibit different catalytic abilities for Cr(VI) photoreduction. It is certain that the photoreduction activities largely depend on the treatment of catalysts. The following factors may influence the Cr(VI) photoreduction efficiency catalysed by layered compounds:

1. Hydration of interlayer [32,33].
2. Formation of reduction site [34,35].
3. Change in excitation energy of the titanate layers [36].
4. Formation of a well defined structure [37].

Hydration of layer is a very important factor influencing the efficiency of Cr(VI) photoreduction. The transfer of Cr(VI) is more feasible in the interlayer of H^+ exchanged layered compounds than that of layered compounds with rigid structure since the H^+ exchanging lead the hydration of layer and flexible structure and large interlayer space are hereby acquired. Moreover, it makes the reduction site in the interlayer of H^+ exchanged layered compound accessible.

H_2 production efficiency catalysed by most layered compounds is increased after layer compound acid exchanged. It was proposed that the acid exchanging enhances the production of reduction sites in the interlayer of layered compounds. Meanwhile, Cr(VI) photoreduction is feasible

Table 1
The adsorption capacity (mg/g) of layered compounds for Cr(VI)

Samples	$K_2Ti_4O_9$	H^+–$K_2Ti_4O_9$ (423 K)	H^+–$K_2Ti_4O_9$ (623 K)
Adsorption amount (mg/g)	0.550	0.835	0.535

Table 2
The rate constants of Cr(VI) photoreduction in the presence and absence of catalysts

Rate constants ($\times 10^{-8}$)	pH=1.0	pH=2.0	Rate constants at different solution pH value
Cat. free ($M^{1/2} s^{-1}$)	165	82.6	1:0.498
TiO_2 ($M^{1/2} s^{-1}$)	254	125	1:0.522
$K_2Ti_4O_9$ ($M^{1/2} s^{-1}$)	6.12	3.11	1:0.508
H^+–$K_2Ti_4O_9$ (423 K) ($M s^{-1}$)	6.67	4.71	1:0.707
H^+–$K_2Ti_8O_{17}$ ($M s^{-1}$)	6.86	5.42	1:0.790

under pH environment because of the shift to anode value of Cr(VI) with increasing solution pH (98 mV per unit). Acid exchanging increases the acidity of layered compounds and produces acid environment which can favour Cr(VI) photoreduction.

Acid exchanging and different layers also lead to a change in the excitation energy of layers. Both acid exchanging and condensation of layers leads red-shift of band gap of layered compounds. Increased light absorption and possible high quantum efficiency is available due to their small band gaps.

High quantum is not only dependent on the light adsorption efficiency. Low recombination of electron and hole, which is excited by band gap radiation, contributes to the high quantum. Formation of well defined structure is of importance to effectively separate the photoexcited charges and eliminate the recombination of excited electron and hole.

$K_2Ti_4O_9$ without further treatment has rigid dimensional structure, its band gap is the largest of all three samples, which means the relatively lower efficiency of light absorption. Cr(VI) is rather difficult to transfer into its interlayer, also there is not any acidic site, maybe reduction site, in the interlayer of $K_2Ti_4O_9$. All these factors lead to the lowest photocatalytic efficiency.

H^+–$K_2Ti_4O_9$ have rather flexible structure which is apt to the transfer for Cr(VI) in the interlayer of layered compound. The diversify of acidic sites in the interlayer of H^+–$K_2Ti_4O_9$ also enhance its photocatalytic efficiency.

H^+–$K_2Ti_8O_{17}$ shows the smallest excitation gap and largest light absorption efficiency of three-layered compounds. Meanwhile, the well defined structure can be obtained by further treatment at high temperature and therefore, determines the photocatalytic efficiency highest of three-layered compounds. It can be suggested that the high UV absorption efficiency plays a key role in obtaining high catalytic efficiency for Cr(VI) photoreduction.

For different layered compounds, the dependence of their rate constant on the solution pH value is different. Acid exchanging and heating at high temperature alleviate the dependent effect, it is indicated that H^+–$K_2Ti_8O_{17}$ and H^+–$K_2Ti_4O_9$ (423 K) obtain high catalytic activity for Cr(VI) photoreduction and can only be slightly influenced by the change of reaction condition.

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