Preparation and characterization of SiO2-pillared H2Ti4O9 and its photocatalytic activity for methylene blue degradation

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Abstract

SiO2 pillared layered titanate (SiO2–H2Ti4O9) was prepared via intercalating organosilanes into the interlayers of the layered K2Ti4O9 followed by calcination at 500 °C. The resulting materials were characterized using XRD, N2 adsorption–desorption isotherms, UV–vis spectra, IR spectroscopy and Raman spectroscopy. The photocatalytic activity of SiO2–H2Ti4O9 was evaluated by photocatalytic degradation of aqueous methylene blue dye (MB). XRD and specific surface area results showed that SiO2–H2Ti4O9 had an interlayer distance of 1.45 nm and a specific surface area of 148 m2 g−1. UV–vis absorption spectrum of SiO2–H2Ti4O9 showed a red shift, indicative of a narrower band gap compared to K2Ti4O9. In addition, SiO2–H2Ti4O9 showed higher MB adsorption capacity compared to H2Ti4O9 and K2Ti4O9. MB photodegradation over H2Ti4O9, K2Ti4O9 and SiO2–K2Ti4O9 followed zero-order kinetics under our experimental conditions, and the photocatalytic activity of SiO2–H2Ti4O9 was found to be three times higher than that of K2Ti4O9, which could be attributed to the increase of interlayer space and specific surface area of SiO2-pillared layered titanate.

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1. Introduction

The abatement of environmental pollutants using photocatalytic techniques has attracted considerable attention [1–4]. Typical semiconductors, such as TiO2, ZnO, CdS, etc. are usually adopted as effective catalysts in photocatalytic procedures. Recently, novel metal oxide semiconductors with layered structure have been found to be especially active in photocatalytic water splitting to generate H2 and O2 [5–8]. The high catalytic efficiency is generally attributed to the effective separation of photo-generated electron–hole pairs in the interlayers of the layered compounds [9]. In parallel, the layered compounds could be used as effective photocatalysts to remove environmental pollutants. For example, Zheng et al. [10] studied the photocatalytic reduction of aqueous Cr(VI) and concluded that H+–K2Ti4O9 showed higher catalytic activity compared to K2Ti4O9. Paek et al. [11] compared the photocatalytic properties of hydronium intercalated and cation substituted layered titanates and found that hydronium intercalated titanate showed enhanced photocatalytic activity and Fe- and Ni-substituted titanates were active for methylene blue degradation under visible light irradiation.

It is noteworthy that most organic pollutants cannot penetrate into the interlayer space of the layered compound because of its narrow interlayer distance and rigid layered structure due to the high charge density of layers. Therefore, photocatalytic reaction can only occur on the external surface of the layered compound, which eventually leads to a low photocatalytic activity of the layered compound. The pillaring of layered compounds using inorganic oxide clusters is one of the efficient approaches to prepare the stable photocatalyst with enhanced photocatalytic activity by increasing the interlayer space. Lee et al. [12] studied the photocatalytic activity of TiO2–pillared layered titanate for 4-chlorophenol degradation and observed the enhanced photocatalytic degradation efficiency compared with the layered titanate. Choy et al. [13] studied water splitting over TiO2–pillared layered titanate and attributed its high photocatalytic activity to the effective suppression of electron–hole recombination. Wu et al. [14] investigated the photocatalytic decomposition of methyl orange over Fe2O3 pillared layered H2La2Ti3O10 under visible light irradiation and found that Fe2O3–H2La2Ti3O10 exhibited a higher photocatalytic activity compared to that of H2La2Ti3O10. It should be pointed out that for most pillared layered compounds previously reported the inorganic pillars, such as TiO2, Fe2O3, are generally photocatalytically active [12–17]. Therefore, it is technically challenging to clearly clarify the intrinsic roles of the layers in the photocatalytic reaction using pillared layered compounds as photocatalysts.

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In this study, pillared layered titanate with photocatalytically inert SiO$_2$ as the pillar was prepared using K$_2$Ti$_4$O$_9$ as the precursor in order to evaluate the photo catalytic properties of the layers of the pillared layered titanate and its photocatalytic activity was investigated. Methylene blue (MB), one of the most used organic dyes, was selected as the typical organic pollutant to evaluate the photocatalytic behaviors of SiO$_2$–pillared layered titanate.

2. Experimental

2.1. Preparation of catalysts

All chemicals were of analytical grade and were used as received. K$_2$Ti$_4$O$_9$ was prepared by heating a mixture of K$_2$CO$_3$ and TiO$_2$ in a molar ratio of 1:3.5 at 800 °C for 20 h, followed by another 20 h at 800 °C with intermittent grinding. H$_2$Ti$_4$O$_9$ was prepared from K$_2$Ti$_4$O$_9$ by acid exchanging with HCl solution. Typically, 2 g of K$_2$Ti$_4$O$_9$ was suspended in 300 ml of 1 M HCl solution at 45 °C for 3 day. In order to achieve complete ion exchanging HCl solution was intermittently replaced every 24 h. H$_2$Ti$_4$O$_9$ was obtained by repeatedly washing with distilled water and drying at 50 °C.

Organic amine intercalated H$_2$Ti$_4$O$_9$ and SiO$_2$ intercalated H$_2$Ti$_4$O$_9$ was prepared by modifying the method described by Sumida et al. and Wang et al. [18,19]. For the preparation of organic amine preintercalated H$_2$Ti$_4$O$_9$, 1 g of H$_2$Ti$_4$O$_9$ was added into a mixture containing 20 ml of ethanol and dodecylamine (1:1; v/v) which was then transferred to a Teflon-lined stainless autoclave and was heated at 130 °C for 72 h. After cooled to room temperature, the product was recovered by filtration and repeated washing with distilled water, ethanol and drying at 50 °C.

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Scheme 1. Preparation process of SiO$_2$ pillared layered titanate.

2.2. Characterization

X-ray diffraction (XRD) patterns were collected in a Rigaku D/max-RA powder diffraction-meter using Cu K$_{\alpha}$ radiation. The specific surface areas of the samples were determined by N$_2$ adsorption on a Micrometrics ASAP 2020 apparatus at 77 K. FT-IR spectra were recorded on a Nexus 870 FT-IR spectrometer in the range of 400–4000 cm$^{-1}$. The UV–vis spectra of samples were obtained in SHIMAD UV-2401PC UV–vis spectrometer using BaSO$_4$ as a reference. Raman spectra of samples were recorded on the JY HR-800 instrument.

2.3. MB adsorption

For MB adsorption kinetics, 10 ml of distilled water was first mixed with 400 mg of adsorbent in a 1000 ml conical flask for about 10 min. Then, 990 ml of 18 mg l$^{-1}$ MB solution was quickly introduced into the conical flask and the conical flask was strongly shaken in a shaker (THZ-82) in which the adsorption temperature was kept at 25 °C. 10 ml of sample was withdrawn from the flask at preset time intervals. After fast filtration, the residual MB concentration in the solution was determined spectrophotometrically and the adsorption amount was calculated according to the following equation:

$$q_t = \frac{(C_0 - C_t)V}{M}$$  (1)

where $q_t$ is the adsorption amount at time $t$ (mg g$^{-1}$), $C_0$ is the initial concentration of NPEO solution (mg l$^{-1}$), $C_t$ is NPEO concentration (mg l$^{-1}$) at time $t$, $V$ is the volume of NPEO solution (l), and $M$ is the mass of adsorbent (g).

Static MB adsorption on K$_2$Ti$_4$O$_9$, H$_2$Ti$_4$O$_9$ and SiO$_2$–H$_2$Ti$_4$O$_9$ were determined using batch adsorption tests. For pH effect on MB adsorption, MB adsorption on the catalysts was investigated in a pH range ranging from 3 to 11. Typically, a series of Teflon-line capped glass tubes containing 0.15 g of the catalyst and 50 ml of 15 mg l$^{-1}$ MB solution with different pH were shaken in an incubator at 25 °C for 24 h. The adsorbent particles were removed by filtration and the residual MB concentration in the solution was determined using UV–vis spectrometer. The equilibrium adsorption amount of MB was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e)V}{M}$$  (2)

where $q_e$ is the equilibrium adsorption amount (mg g$^{-1}$), $C_0$ is the initial MB concentration (mg l$^{-1}$), $C_e$ is the equilibrium concentra-
tion (mg l\(^{-1}\)), \(V\) is the volume of MB solution (l) and \(M\) is the mass of the catalyst (g).

For the measurement of MB adsorption isotherms, 0.05 g of catalyst was introduced into a 50 ml Teflon-line capped glass tube containing 50 ml of aqueous MB solution with varied initial concentrations. These tubes were transferred into an incubator, in which the adsorption temperature was held at 25 °C. Under continuous shaking, the adsorption process was allowed to last 24 h to reach the adsorption equilibrium. The catalyst powders were removed by centrifugation and the residual concentrations of MB in the solution were determined spectrophotometrically. The equilibrium adsorption amount of MB was calculated according to Eq. (2).

### 2.4. Photocatalytic activity

The photocatalytic activities of the catalysts for MB degradation were evaluated in a Pyrex reactor equipped with a 500 ml thermostatted cylindrical Pyrex vessel which was irradiated directly by a medium pressure mercury lamp (250 W). For a typical run, 0.2 g of catalyst was suspended in 500 ml of 50 mg l\(^{-1}\) MB solution in the dark for 60 min in order to reach the adsorption equilibrium prior to the photo-degradation experiment. During the photocatalytic reaction, samples were collected at selected time intervals. The catalyst powders were removed by centrifugation and the residual concentration of MB was determined spectrophotometrically.

### 3. Results and discussion

#### 3.1. Catalysts characterization

Fig. 1 shows the XRD patterns of K\(_2\)Ti\(_4\)O\(_9\), H\(_2\)Ti\(_4\)O\(_9\), dodecylamine–H\(_2\)Ti\(_4\)O\(_9\), TEOS–H\(_2\)Ti\(_4\)O\(_9\) and SiO\(_2–\)H\(_2\)Ti\(_4\)O\(_9\). The XRD patterns of experimentally prepared K\(_2\)Ti\(_4\)O\(_9\) and H\(_2\)Ti\(_4\)O\(_9\) were found to be in good agreement with the standard XRD patterns of K\(_2\)Ti\(_4\)O\(_9\) (JCPDS: 27-0447) and H\(_2\)Ti\(_4\)O\(_9\)·H\(_2\)O (JCPDS: 36-0655). In parallel, the characteristic interlayer spaces of K\(_2\)Ti\(_4\)O\(_9\) and H\(_2\)Ti\(_4\)O\(_9\) calculated based on (2 0 0) diffraction peak prior to the photo-degradation experiment. During the photocatalytic reaction, samples were collected at selected time intervals. The catalyst powders were removed by centrifugation and the residual concentration of MB was determined spectrophotometrically. The significantly larger interlayer space of dodecylamine–H\(_2\)Ti\(_4\)O\(_9\) is mainly attributed to the intercalation of H\(_3\)O\(^+\) into the interlayers. Hydrothermal reaction of H\(_2\)Ti\(_4\)O\(_9\) with dodecylammonium led to a substantial shift of (2 0 0) diffraction peak toward low 2\(\theta\) angle corresponding to an interlayer space of 3.32 nm, demonstrating the intercalation of dodecylamine into the interlayer of H\(_2\)Ti\(_4\)O\(_9\). This conclusion is further supported by IR analysis. IR bands of dodecylamine intercalated H\(_2\)Ti\(_4\)O\(_9\) is compiled in Fig. 1b. IR bands at 2930 cm\(^{-1}\) and 2858 cm\(^{-1}\) were characteristic of methylene stretching vibration. IR band at 1468 cm\(^{-1}\) was assigned to methylene deformation vibration. Deformation vibration of NH\(^+\) groups was observed at 1559 cm\(^{-1}\) [20]. These results clearly demonstrate the intercalation of dodecylamine into the interlayers of H\(_2\)Ti\(_4\)O\(_9\).

After exchanging with TEOS, (2 0 0) diffraction peak characteristic of dodecylamine–H\(_2\)Ti\(_4\)O\(_9\) was not observed and a new diffraction peak characteristic of (2 0 0) diffraction of TEOS–H\(_2\)Ti\(_4\)O\(_9\) was visible (see Fig. 1d). Compared with dodecylamine–H\(_2\)Ti\(_4\)O\(_9\), (2 0 0) diffraction peak of TEOS–H\(_2\)Ti\(_4\)O\(_9\) was shifted to slightly high 2\(\theta\) angle, corresponding to an interlayer space of 2.54 nm. This suggests that TEOS is capable of penetrating into the interlayers and the majority of dodecylamine in the interlayers of H\(_2\)Ti\(_4\)O\(_9\) is replaced by TEOS during the exchanging reaction. After TEOS exchanging, calcination is a general approach to remove all organic species and to obtain the stable inorganic pillars. Upon calcination at 500 °C, (2 0 0) diffraction peak shifted to high 2\(\theta\) angle corresponding to an interlayer space of 1.45 nm. The decreased interlayer distance of SiO\(_2–\)H\(_2\)Ti\(_4\)O\(_9\) can be attributed to the decomposition of organic species in the interlayer. This is also in agreement with IR results. Fig. 2b shows the IR spectra of SiO\(_2–\)H\(_2\)Ti\(_4\)O\(_9\). The IR bands at 830 cm\(^{-1}\) and 1070 cm\(^{-1}\) are ascribed to the Si–O–Si stretching vibration and IR band at 491 cm\(^{-1}\) is characteristic of Si–O–Si bending vibration and IR band at 962 cm\(^{-1}\) is assigned to Si–OH bending vibration [21]. Note that IR absorption characteristic of C–H stretching and bending vibrations was not observed, indicating that calcination at 500 °C leads to the complete decomposition of organic species and the formation of inorganic silica pillars in

### Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Interlayer space (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(_2)Ti(_4)O(_9)</td>
<td>0.88</td>
</tr>
<tr>
<td>H(_2)Ti(_4)O(_9)</td>
<td>0.92</td>
</tr>
<tr>
<td>Dodecylamine–H(_2)Ti(_4)O(_9)</td>
<td>3.32</td>
</tr>
<tr>
<td>TEOS–H(_2)Ti(_4)O(_9)</td>
<td>2.54</td>
</tr>
<tr>
<td>SiO(_2–)H(_2)Ti(_4)O(_9)</td>
<td>1.45</td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns of (a) K\(_2\)Ti\(_4\)O\(_9\), (b) H\(_2\)Ti\(_4\)O\(_9\), (c) dodecylamine–H\(_2\)Ti\(_4\)O\(_9\), (d) TEOS–H\(_2\)Ti\(_4\)O\(_9\) and (e) SiO\(_2–\)H\(_2\)Ti\(_4\)O\(_9\).

Fig. 2. IR spectra of (a) dodecylamine–H\(_2\)Ti\(_4\)O\(_9\) and (b) SiO\(_2–\)H\(_2\)Ti\(_4\)O\(_9\).
the interlayers. For H$_2$Ti$_4$O$_9$, calcination generally leads to the condensation of titanate layers and to the generation of anatase TiO$_2$ [10]. The absence of anatase TiO$_2$ in SiO$_2$–H$_2$Ti$_4$O$_9$ after calcination at 500 °C is mainly attributed to the separation of titanate layers by SiO$_2$ pillars, which effectively suppresses the condensation occurring between titanate layers. This also implies that the layer structure is retained during pillaring and calcination processes.

N$_2$ adsorption–desorption isotherms of K$_2$Ti$_4$O$_9$, H$_2$Ti$_4$O$_9$ and SiO$_2$–H$_2$Ti$_4$O$_9$ are compared in Fig. 3 and the specific surface areas and pore volumes of these materials are listed in Table 2. The specific surface areas of K$_2$Ti$_4$O$_9$ and H$_2$Ti$_4$O$_9$ were 5.4 and 30.8 m$^2$ g$^{-1}$ respectively, whereas the specific surface area of the SiO$_2$–H$_2$Ti$_4$O$_9$ was found to be 148.0 m$^2$ g$^{-1}$, which is markedly higher compared to K$_2$Ti$_4$O$_9$ and H$_2$Ti$_4$O$_9$. Total pore volumes of K$_2$Ti$_4$O$_9$, H$_2$Ti$_4$O$_9$ and SiO$_2$–H$_2$Ti$_4$O$_9$ were found to be 0.0097, 0.058 and 0.194 cm$^3$ g$^{-1}$, respectively. In addition, the micropore volume of SiO$_2$–H$_2$Ti$_4$O$_9$ was 0.019 cm$^3$ g$^{-1}$, whereas micropores were absent in K$_2$Ti$_4$O$_9$ and H$_2$Ti$_4$O$_9$. The increase specific surface area of SiO$_2$–H$_2$Ti$_4$O$_9$ and the presence of micropores in SiO$_2$–H$_2$Ti$_4$O$_9$ exclusively resulted from the pillaring of H$_2$Ti$_4$O$_9$ layers by SiO$_2$ pillars.

The UV–vis absorption spectra of K$_2$Ti$_4$O$_9$, H$_2$Ti$_4$O$_9$ and SiO$_2$–H$_2$Ti$_4$O$_9$ are compared in Fig. 4a. The absorption threshold of K$_2$Ti$_4$O$_9$ was approximately 334 nm, whereas the absorbance spectra of H$_2$Ti$_4$O$_9$ and SiO$_2$–H$_2$Ti$_4$O$_9$ were red shifted by about 40 nm, indicative of narrower band gaps of H$_2$Ti$_4$O$_9$ and SiO$_2$–H$_2$Ti$_4$O$_9$ compared to K$_2$Ti$_4$O$_9$. In principle, semiconductor can be classified into direct or indirect one based on its electric transition nature. In the case of a direct semiconductor, the optical absorbance can be described as follows [22]:

$$\alpha h\nu = B(h\nu - E_g)^{1/2}$$

where $\alpha$ is absorbance coefficient, $B$ is absorbance constant, $E_g$ is band gap and $\nu$ is light frequent, respectively.

The plot of $(\alpha h\nu)^2$ versus $h\nu$ is shown in Fig. 4b. $E_g$ is equal to the intercept of linear extrapolation to $h\nu$ axis and the obtained $E_g$ values for K$_2$Ti$_4$O$_9$, H$_2$Ti$_4$O$_9$ and SiO$_2$–H$_2$Ti$_4$O$_9$ are found to be 3.96, 3.44 and 3.52 eV, respectively. Huang et al. [6] studied layered K$_{2-x}$La$_2$Ti$_{3-x}$Nb$_x$O$_{10}$ and their protonated derivatives and also observed the larger band gap of K$_{2-x}$La$_2$Ti$_{3-x}$Nb$_x$O$_{10}$ compared to protonated derivatives. The larger band gap of SiO$_2$–H$_2$Ti$_4$O$_9$ compared to H$_2$Ti$_4$O$_9$ probably results from calcination of SiO$_2$–H$_2$Ti$_4$O$_9$ at high temperature and effective separation of titanate layers by SiO$_2$ pillaring [10].

The Raman spectra of K$_2$Ti$_4$O$_9$, H$_2$Ti$_4$O$_9$ and SiO$_2$–H$_2$Ti$_4$O$_9$ were depicted in Fig. 5. The observed Raman peaks at 622, 663 cm$^{-1}$ were attributed to the Ti–O stretching vibrations of TiO$_6$ octahedra. The bands in the 872 cm$^{-1}$ were characteristic of typical protonated titanate [23,24]. After acid exchanging, marked changes were observed. The Raman bands at 395, 458, 679 and 869 cm$^{-1}$ were characteristic of typical protonated titanate [25] and the peak at 264 cm$^{-1}$ was assigned to Ti–OH bonds [26]. SiO$_2$ pillaring led to the weakening of Raman intensity and slight shift of Raman peaks, possibly resulting from the changes in morphology and particle size during the pillaring process [27,28].

**Table 2**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Specific surface area (m$^2$ g$^{-1}$)</th>
<th>Micropore volume (cm$^3$ g$^{-1}$)$^a$</th>
<th>Total pore volume (cm$^3$ g$^{-1}$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$Ti$_4$O$_9$</td>
<td>5.4</td>
<td>0</td>
<td>0.0097</td>
</tr>
<tr>
<td>H$_2$Ti$_4$O$_9$</td>
<td>30.8</td>
<td>0</td>
<td>0.058</td>
</tr>
<tr>
<td>SiO$_2$–H$_2$Ti$_4$O$_9$</td>
<td>148.0</td>
<td>0.019</td>
<td>0.194</td>
</tr>
</tbody>
</table>

$^a$ Micropore volume is determined by the t-plot method using N$_2$ adsorption isotherm.

$^b$ Total pore volume is determined at $P/P_0 = 0.98$. 

**3.2. MB adsorption on the catalysts**

In principle, the catalytic reaction mainly occurs on photocatalyst surface in a heterogeneous photocatalytic reaction system and
reactant adsorption on catalyst surface is generally believed to be a prerequisite step. Therefore, MB adsorption over the catalysts may play an important role in MB photo-catalytic degradation.

The time-resolved uptakes of MB over \( \text{H}_2\text{Ti}_4\text{O}_9 \), \( \text{K}_2\text{Ti}_4\text{O}_9 \) and \( \text{SiO}_2—\text{H}_2\text{Ti}_4\text{O}_9 \) are shown in Fig. 6. For all samples, MB adsorption quickly reached the equilibrium within 10 min. In addition, MB adsorption amount of \( \text{SiO}_2—\text{H}_2\text{Ti}_4\text{O}_9 \) was higher than those of \( \text{H}_2\text{Ti}_4\text{O}_9 \), \( \text{K}_2\text{Ti}_4\text{O}_9 \). The influence of pH on MB adsorption on the catalysts is compared in Fig. 7. Similarly, a markedly higher MB adsorption amount on \( \text{SiO}_2—\text{H}_2\text{Ti}_4\text{O}_9 \) was observed compared to \( \text{H}_2\text{Ti}_4\text{O}_9 \), \( \text{K}_2\text{Ti}_4\text{O}_9 \). For all catalysts, increasing solution pH led to increased MB adsorption, which is attributed to the increased electrostatic interaction of MB with the catalysts [29].

MB adsorption isotherms on the \( \text{K}_2\text{Ti}_4\text{O}_9 \), \( \text{H}_2\text{Ti}_4\text{O}_9 \) and \( \text{SiO}_2—\text{H}_2\text{Ti}_4\text{O}_9 \) at 25°C and pH 6.5 are presented in Fig. 8. The adsorption behaviors of MB on the catalysts were described using the Langmuir adsorption model [30]:

\[
q_e = \frac{q_\infty b C_e}{(1 + b C_e)}
\]

(4)

where \( q_e \) is the equilibrium adsorption amount, \( q_\infty \) the maximum adsorption amount, \( b \) the adsorption constant and \( C_e \) the equilibrium concentration of MB, respectively.

Fitting results showed that MB adsorption on the catalysts could be well described by Langmuir adsorption model with \( R^2 \) larger than 0.95 and the resulting parameters are listed in Table 3. The maximum adsorption capacities of \( \text{K}_2\text{Ti}_4\text{O}_9 \), \( \text{H}_2\text{Ti}_4\text{O}_9 \) and \( \text{SiO}_2—\text{H}_2\text{Ti}_4\text{O}_9 \) for MB were found to be 4.8, 8.1 and 21.6 mg g\(^{-1}\), respectively. The higher MB adsorption capacity of \( \text{H}_2\text{Ti}_4\text{O}_9 \) mainly results from the higher specific surface area of \( \text{H}_2\text{Ti}_4\text{O}_9 \) compared to \( \text{K}_2\text{Ti}_4\text{O}_9 \). In comparison with \( \text{H}_2\text{Ti}_4\text{O}_9 \) and \( \text{K}_2\text{Ti}_4\text{O}_9 \), \( \text{SiO}_2 \) pillaring further enhances MB adsorption due to the higher specific surface area of \( \text{SiO}_2—\text{K}_2\text{Ti}_4\text{O}_9 \). Note that the interlayer space of \( \text{SiO}_2—\text{K}_2\text{Ti}_4\text{O}_9 \) is 1.45 nm, which is larger compared to the kinetic diameter of MB molecule (1.41 nm × 0.55 nm × 0.16 nm [31]). Therefore, the interlayer space of \( \text{SiO}_2—\text{H}_2\text{Ti}_4\text{O}_9 \) is accessible for MB molecule. It should be further pointed out that molecules adsorbed on catalyst surface are prone to photocatalytic reaction as heterogeneous photocatalysis is generally believed to be an interfacial process. In addition, only molecules adsorbed on photocatalytically active sites of the photocatalyst tend to undergo

**Table 3**

Fitting parameters of MB adsorption isotherms over the samples using Langmuir adsorption model.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( q ) (mg g(^{-1}))</th>
<th>( b ) (lmg(^{-1}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{K}_2\text{Ti}_4\text{O}_9 )</td>
<td>4.8</td>
<td>0.11</td>
<td>0.98</td>
</tr>
<tr>
<td>( \text{H}_2\text{Ti}_4\text{O}_9 )</td>
<td>8.1</td>
<td>0.12</td>
<td>0.99</td>
</tr>
<tr>
<td>( \text{SiO}_2—\text{H}_2\text{Ti}_4\text{O}_9 )</td>
<td>21.6</td>
<td>0.61</td>
<td>0.99</td>
</tr>
<tr>
<td>( \text{SiO}_2 )</td>
<td>5.9</td>
<td>0.14</td>
<td>0.95</td>
</tr>
</tbody>
</table>
directly photocatalytic degradation. For SiO$_2$–H$_2$Ti$_4$O$_9$, SiO$_2$ is introduced into the interlayers as photocatalytically inert inorganic pillar and MB adsorption on SiO$_2$ surface may contribute to the increased MB adsorption. Therefore, MB adsorption on SiO$_2$ was investigated in order to clarify MB adsorption sites in SiO$_2$–H$_2$Ti$_4$O$_9$. As shown in Fig. 8, the maximum adsorption of SiO$_2$ for aqueous MB is lower than 6 mg g$^{-1}$, which is substantially lower compared to that on SiO$_2$–H$_2$Ti$_4$O$_9$. This clearly indicates that the majority of MB molecules are adsorbed on the layer surface of SiO$_2$–H$_2$Ti$_4$O$_9$, which may result in the significant difference in its photocatalytic properties. It is also noteworthy that the constants $(b)$ of MB adsorption differ in the catalysts. In principle, Langmuir adsorption constant $b$ is characteristic of the affinity of adsorbate to adsorbent [32,33]. The identical adsorption constant of H$_2$Ti$_4$O$_9$ to that of K$_2$Ti$_4$O$_9$ suggests similar adsorption strength possibly due to MB adsorption on the external surfaces of H$_2$Ti$_4$O$_9$ and K$_2$Ti$_4$O$_9$. The markedly higher adsorption constant of SiO$_2$–H$_2$Ti$_4$O$_9$ can be attributed to MB adsorption in the micropores due to the higher adsorption force field compared to non-porous surface [34].

### 3.3. Photocatalytic activity

In order to study pH influence on photocatalytic MB degradation, photocatalytic MB degradation on SiO$_2$–H$_2$Ti$_4$O$_9$ was investigated at pH of 4.7, 6.5 and 9.7. After irradiation for 1 h, MB with initial concentration of 50 mg l$^{-1}$ was removed by 63.8, 64.0 and 48.1% at pH of 4.7, 6.5 and 9.7, suggesting that MB can be facilely degraded at neutral and acidic conditions. Therefore, photocatalytic MB degradation was only conducted at pH of 6.5. The photocatalytic degradation of aqueous MB over K$_2$Ti$_4$O$_9$, H$_2$Ti$_4$O$_9$ and SiO$_2$–H$_2$Ti$_4$O$_9$ is compiled in Fig. 9a. After irradiation for 60 min, MB was found to be removed by 16.2, 20.7 and 64.0% over K$_2$Ti$_4$O$_9$, H$_2$Ti$_4$O$_9$ and SiO$_2$–H$_2$Ti$_4$O$_9$, respectively, suggesting that the photocatalytic activities for MB decrease according to SiO$_2$–H$_2$Ti$_4$O$_9$ > H$_2$Ti$_4$O$_9$ > K$_2$Ti$_4$O$_9$.

The fitting results showed that the kinetics of MB photodegradation catalyzed by the catalysts could be well described as zero-order kinetics:

$$ r = -\frac{dC}{dt} = k $$

where $r$ is the reaction rate, $C_t$ the concentration of MB at reaction time $t$, $C_0$ the initial concentration of MB and $k$ the reaction rate constant, respectively.

In principle, catalytic MB photodegradation is an interface process following Langmuir–Hinshelwood model [35,36]:

$$ r = -\frac{dC}{dt} = \frac{kbC}{(1 + bC)} $$

$$ r = -\frac{dC}{dt} = k \quad bC \gg 1 $$

$$ r = -\frac{dC}{dt} = kbC \quad bC \ll 1 $$

where $r$ is the reaction rate, $C$ is MB concentration, $k$ the reaction rate constant and $b$ is the adsorption constant, respectively.

For MB adsorption over K$_2$Ti$_4$O$_9$, H$_2$Ti$_4$O$_9$ and SiO$_2$–H$_2$Ti$_4$O$_9$, $bC$ values are found to be 5.5, 5.0 and 30.1 at MB equilibrium concentration of 50 mg l$^{-1}$, which are markedly higher than 1. Provided photocatalytic MB degradation follows Langmuir–Hinshelwood model, MB degradation can be described using zero-order kinetics, which is in good agreement with our experimental results. In order to clarify MB degradation kinetics, catalytic MB photodegradation was investigated at varied initial concentrations. As shown in Fig. 9b, MB degradation rates constants were found to be 0.42, 0.42 and 0.43 mg l$^{-1}$ min$^{-1}$ at initial MB concentration of 50, 35 and 31 mg l$^{-1}$, indicative of the independence of MB photodegradation rate on initial MB concentration. This further suggests that MB degradation follows Langmuir–Hinshelwood model.

The reaction rate constants could be obtained by fitting the experimental data using zero-order reaction kinetics and the rate constants of K$_2$Ti$_4$O$_9$, H$_2$Ti$_4$O$_9$ and SiO$_2$–H$_2$Ti$_4$O$_9$ for MB degradation were 0.13, 0.15 and 0.43, respectively. The resulting $R^2$ values were higher than 0.99, suggesting that MB photodegradation catalyzed by K$_2$Ti$_4$O$_9$, H$_2$Ti$_4$O$_9$ and SiO$_2$–H$_2$Ti$_4$O$_9$ can be well described by zero-order reaction kinetics. In comparison with K$_2$Ti$_4$O$_9$, H$_2$Ti$_4$O$_9$ exhibits a slightly higher catalytic activity probably due to its higher specific surface. For SiO$_2$–H$_2$Ti$_4$O$_9$ the reaction rate constant is 0.43 mg l$^{-1}$ min$^{-1}$, approximately three times higher than that of H$_2$Ti$_4$O$_9$. For MB photodegradation on K$_2$Ti$_4$O$_9$ or H$_2$Ti$_4$O$_9$, MB molecules cannot penetrate into the interlayers of K$_2$Ti$_4$O$_9$ or H$_2$Ti$_4$O$_9$ due to the high layer charge and narrow interlayer space. Therefore, MB photocatalytic degradation only occurs on the external surface of K$_2$Ti$_4$O$_9$ and H$_2$Ti$_4$O$_9$, which consequently leads to the low photocatalytic activities. In the case of SiO$_2$–H$_2$Ti$_4$O$_9$, however, SiO$_2$ pillaring results in expanded interlayer space, which is capable of hosting MB molecules, resulting in a markedly higher photocatalytic activity of SiO$_2$–H$_2$Ti$_4$O$_9$ compared to K$_2$Ti$_4$O$_9$ or H$_2$Ti$_4$O$_9$. 

*Fig. 9.* (a) Photocatalytic MB degradation on (●) K$_2$Ti$_4$O$_9$, (▲) H$_2$Ti$_4$O$_9$, (■) SiO$_2$–H$_2$Ti$_4$O$_9$. (b) Influence of MB initial concentration on photocatalytic degradation rates of SiO$_2$–H$_2$Ti$_4$O$_9$. The rate constant is 0.43 mg l$^{-1}$ min$^{-1}$ at initial MB concentration of 50, 35 and 31 mg l$^{-1}$, indicative of the independence of MB photodegradation rate on initial MB concentration. This further suggests that MB degradation follows Langmuir–Hinshelwood model.
4. Conclusions

SiO₂-pillared layered titanate (SiO₂–H₂Ti₄O₉) was prepared from layered K₂Ti₄O₉ by acid exchanging, pre-intercalation by dodecylamine, exchanging reaction with TEOS and calcination. Characterization results show that SiO₂ intercalation leads to the generation of micropores and to substantially elevated specific surface area. The presence of micropores and high specific surface area concomitantly results in the higher MB adsorption capacity and stronger adsorption affinity compared to K₂Ti₄O₉ and H₂Ti₄O₉. In addition, the band gap of SiO₂–H₂Ti₄O₉ is lower compared to K₂Ti₄O₉. The higher photocatalytic activity of SiO₂–H₂Ti₄O₉ is mainly ascribed to the larger interlayer space and higher specific surface area of SiO₂–H₂Ti₄O₉.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 20637030 and 20677026), Scientific and Technical Supporting Programs of China (2006BAC02A15) and the GY project (2007GY026).

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