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# Kinetics of Photocatalytic Degradation of Formic Acid over Silica Composite Films Based on Polyoxometalates

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**Abstract:** The composite films, $XW_{11}O_{39}^{n-}/SiO_2$, (X refers to Si, Ge or P, respectively) were prepared by tetraethoxysilane (TEOS) hydrolysis sol-gel method *via* spin-coating technique. Formation of the composite films is due to strong chemical reaction of organic silanol group with the surface oxygen atoms of $XW_{11}O_{39}^{n-}$, resulted in the saturation of the surface of the lacunary polyoxometalates (POMs). Therefore, the coordination structural model of the films was proposed. As for the films, retention of the primary Keggin structure was confirmed by UV-vis, FT-IR spectra and MAS NMR. The surface morphology of the films was characterized by SEM, indicating that the film surface is relatively uniform, and the layer thickness is in the range of 250~350 nm. Aqueous formic acid (FA) (0-20 mmol/L) was degraded into $CO_2$ and $H_2O$ by irradiating the films in the near-UV area. The results show that all the films have photocatalytic activities and the degradation reaction follows Langmuir-Hinshelwood first order kinetics.

**Keywords:** Polyoxometalates, sol-gel, spin coating, composition film, photocatalysis, kinetics, formic acid.

So far, much work has been done on studying polyoxometalates (POMs) as photocatalysts for photo-oxidation of aqueous pollutants[1]. However, most of such studies are concerned with homogeneous systems[2]. As known, POMs have high water solubility, and it impedes their recovery and reuse. Recently, progress has been made for preparation of desolubilized POM materials[3]. Preparation of POM-containing films is a new way of immobilization of soluble POMs[4]. Among all the synthesis techniques, sol-gel method has obvious feasibility and easy control properties. Furthermore, to our knowledge, little reports have been made on the photocatalytic application of POMs-containing composite films. Here, we prepared $XW_{11}O_{39}^{n-}/SiO_2$ ($XW_{11}/SiO_2$) composite films by sol-gel method *via* spin-coating technique, and the photocatalytic behavior of the films was studied *via* degradation of FA under near-UV irradiation. The purpose of selecting FA as the model substance is that it is an organic pollutant existed in water or a stable intermediate found in photo-degraded processes. Photocatalytic tests showed that all the films have photocatalytic activity and the degradation reaction followed Langmuir-Hinshelwood first order kinetics.

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## Experimental

$XW_{11}/SiO_2$ films were prepared as follows. 1.0 g of $XW_{11}$ was dissolved in water at room temperature (a little amount of dilute $HNO_3$ was added dropwise under vigorous stirring to increase the solubility of the $XW_{11}$). EtOH and TEOS were mixed, and the pH of the mixture was adjusted with dilute $HNO_3$. The acidic TEOS mixture was added to the solution of $XW_{11}$ and the pH should be changed when the different precursors were used. The reaction solution was stirred for *ca.* 1 h until a homogeneous silica sol was obtained. Then the quartz substrate was coated with the $XW_{11}/SiO_2$ sol. The films were dried under nitrogen atmosphere at room temperature. Finally the films were calcinated in vacuum at 120°C for 2 h for further fasten the silica network.

The photoreactor was designed with cylindrical quartz cell configuration and an internal light source surrounded by a quartz jacket, where aqueous FA solution completely surrounded the light source. Two slides ($1.25\times12\times45$ $mm^3$) of the films were placed near the wall of the reactor. An external cooling coil was used to maintain the reaction temperature constant. The light source was a 125 W high pressure mercury lamp (HPML, output mainly at 313.2 nm). A general photocatalytic procedure was as follows. After the intensity of the light source became stable, the lamp was inserted into a fresh aqueous FA solution. The experiments were carried out at $25\pm2$°C with vigorous stirring.

## Results and Discussion

The inorganic precursor $XW_{11}$ (X refers to Si, Ge or P) was introduced onto the quartz substrate in the form of hybrid silica sol $XW_{11}/SiO_2$. During TEOS hydrolysis sol-gel process, lacunary $XW_{11}$ cluster reacted with the products of TEOS hydrolysis $[Si^*(OSi)_4\text{-}n(OH)_n]$, led to the saturation of the $XW_{11}$ surface. Therefore, the coordination structural model of the films was proposed and shown in **Figure 1**. After formation of the composite films, retention of the structure integrity of the starting $XW_{11}$ (X = P, Si, Ge) was confirmed by UV-vis, FT-IR, $^{29}Si$ and $^{31}P$ MAS NMR. Absorption at *ca.* 200 nm and 265 nm in UV spectroscopy was attributed to charge-transfer at W=O and W-O-W bonds, respectively. The UV data for the starting $XW_{11}$ are in agreement with that of the films, suggesting that the primary Keggin frameworks were retained

**Figure 1** Proposed coordination model of the $XW_{11}/SiO_2$ films

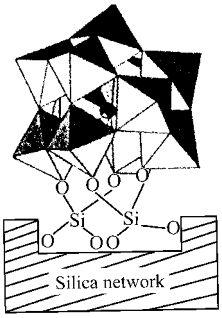


**Table 1** Main IR data ($cm^{-1}$) of the starting $XW_{11}$ and corresponding $XW_{11}/SiO_2$ (X = P, Si, Ge)

| Sample | $\nu$ as (X-O) | $\nu$ as (W=$O_{ter}$) | $\nu$ as (W-O-W) |
|---|---|---|---|
| $PW_{11}$ | 1095, 1043 | 953 | 862,833,805, 730 |
| $PW_{11}/SiO_2$ film | 1079 | 953 | 870, 797, 672 |
| $SiW_{11}$ | 995 | 950 | 882, 796, 728 |
| $SiW_{11}/SiO_2$ film | 1081 | 962 | 804, 697, 626 |
| $GeW_{11}$ | 959 | 882 | 796, 697 |
| $GeW_{11}/SiO_2$ film | 956 | 881 | 792, 733, 676 |

intact after covalent bond with silica network was formed. FT-IR data of the starting $XW_{11}$ and corresponding $XW_{11}/SiO_2$ films are shown in **Table 1**.

Pure $XW_{11}$ display a characteristic infrared fingerprint in the region from *ca.* 1000 to 700 $cm^{-1}$, attributed to X-O in central $XO_4$ unit, W=O and W-O-W vibrations of $XW_{11}$ respectively. In the band of the silica framework at 1080 $cm^{-1}$ covered the vibration band of Si-O from central $SiO_4$ unit of $SiW_{11}$. The presence of the Si-O bond from central $SiO_4$ of $SiW_{11}$ in the films was proved by $^{28}$Si MAS NMR. The resonance at $\delta$ -94.31 ppm originated from central $SiO_4$ unit of $SiW_{11}$ cluster, which is nearly the same with that of the parent $SiW_{11}$ ($\delta$ -93.0 ppm), suggesting that Si-O in central $SiO_4$ existed in the hybrid materials. Therefore, we confirmed that after formation of the composite film the structure integrity of $SiW_{11}$ was in retention. In the case of pure $PW_{11}$, the bands of P-O in central $PO_4$ were at 1095 and 1043 $cm^{-1}$ in IR. However, only one band at 1079 $cm^{-1}$ was observed for the $PW_{11}/SiO_2$ film. At the same time, $^{31}$P MAS NMR showed one resonance signal at $\delta$ -13.5 ppm. These results showed that saturation of the cluster was obtained through grafting of siloxane group (determined $^{31}$P MAS NMR resonance for $PW_{12}$ and $PW_{11}$ was at $\delta$ -12.9 and 10.4 ppm, respectively). W loadings estimated by ICP-AES for $XW_{11}/SiO_2$ films (X= P, Si, Ge) are 9.1%, 8.1%, and 7.6% respectively. In addition, experimental conditions may have effects on W loading. SEM images of $XW_{11}/SiO_2$ films indicate that the $XW_{11}/SiO_2$ sols were really coated on the surface of the quartz slide. The images also show that the as-synthesized films are relatively uniform and the thickness of the films is in the range of 250~350 nm.

The photocatalytic activity of the $XW_{11}/SiO_2$ films is due to $XW_{11}$. The photocatalytic activity of as-synthesized films was tested *via* degradation of an aqueous FA solution under irradiation in the near-UV area. In the presence of the films, stirring the aqueous FA solution in the dark for 120 min, the disappearance of FA is negligible. As for the silica support, *ca.* 6.5 % of FA disappeared under UV-irradiation for 120 min. However, apparent changes in the concentrations of FA were observed by irradiating the FA solutions in the presence of two slides of $XW_{11}/SiO_2$ films, *i.e.*, conversion of FA into $CO_2$ and $H_2O$ was in the range of 50 %~60 % for different slides used (irradiation time was 120 min), as shown in **Figure 2** （Initial concentration of FA was 4 mmol/L）. These results suggest that degradation of FA mainly originated from photoexcitation of the $XW_{11}/SiO_2$ films. Influence of initial FA concentration ($C_0$) on the initial FA disappearance rate ($R_0$) for photodegradation of FA solution was studied, and the results are shown in **Figure 3**. By changing $C_0$ in the range of 0-20 mmol/L, plot of $R_0$ *vs* $C_0$ exhibits three nearly straight lines. The value of k (the reaction rate constant) derived

**Figure 2** Plot of Conversion *vs* Time

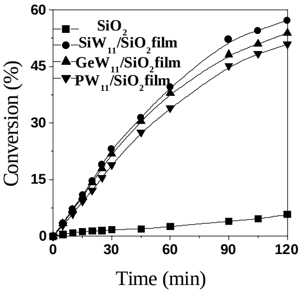
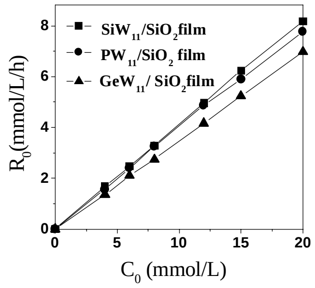


**Figure 3** Initial rate ($R_0$) *vs* initial concentration



were 0.035, 0.029, 0.034 mmol/L/min respectively. The values of K (the adsorption equilibrium constant) are almost the same. The first order linear relationship can be explained in a Langmuir-Hinshelwood model (Eq.1):

$$R = -dC/dt = -kKC/(1 + KC) \qquad \text{(Eq.1)}$$

As for dilute solution, KC«1, therefore, the above model can be expressed by (Eq.2):

$$R_0=KkC_0 \qquad \text{(Eq.2)}$$

Indicating that the disappearance of FA follows a Langmuir-Hinshelwood first order kinetic law for initial FA concentration.

## Conclusion

The method of preparation of the silica composite films based on lacunary Keggin-type POMs was proposed for the first time. The primary Keggin structures remained intact after formation of the films. Under UV-irradiation, all as-synthesized films exhibited photocatalytic activity on the degradation of aqueous FA. Little leakage of the POM from the silica matrix was due to chemical grafting of organosiloxane units to the surface of the lacunary POM. The films are more easily handled than that of the powder photocatalytic materials. The method exhibits the potential for practical applications.

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