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Photocatalysis of dinitrotoluene decomposition by $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$ prepared by a modified sol-gel synthesis and solvothermal treatment method

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ABSTRACT

Mesoporous $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$ were synthesized by combining sol-gel technology using a nonionic surfactant P123 as a structure directing agent with solvothermal treatment. X-ray diffraction and Raman spectroscopy results indicated that the TiO_2 particles had the anatase phase, and the primary Keggin structures of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ remained intact after calcination at 400 °C. N_2 adsorption-desorption analysis and scanning electron microscopy showed that the specific surface area and pore volume were increased by the addition of P123. The specific surface area of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$ increased to 252.2 and 250.0 m^2/g , respectively. Ultraviolet-visible absorption spectroscopy showed that compared with pure TiO_2 , an obvious red shift occurred and the absorption intensity was increased for the composite catalysts. The catalysts were tested and the degradation rate of dinitrotoluene was as high as 95% under the optimum conditions.

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1. Introduction

Dinitrotoluene (DNT) is an intermediate product in the manufacture of 2,4,6-trinitrotoluene and a precursor of toluene diisocyanate used for the preparation of polyurethane foams. Both 2,4-DNT and 2,6-DNT are priority pollutants due to their toxicity and possible carcinogenicity. Therefore, the degradation of DNT in wastewater has gained much attention. In the study of Chen et al. [1–3], Fenton's reagent, O_3 , and UV/O_3 were used to mineralize DNT isomers in spent acid from a toluene nitration process. Several researchers [4–7] have focused on the degradation of nitroaromatic compounds by $\text{UV}/\text{Fenton's reagent}$ or a $\text{UV}/\text{H}_2\text{O}_2$ technique. The development of an effective and inexpensive decontamination technology for explosive

wastewaters is of continuing interest.

The photocatalytic degradation of DNT has been considered an emerging promising method. It can decompose most organic pollutants and mineralize them to CO_2 , H_2O , and other small inorganic molecules completely. Feng and coworkers [8–10] reported that as a photocatalyst, POMs/ TiO_2 (POM: polyoxometalate) exhibited excellent activity in photocatalyzing the decomposition of various organic contaminants, including dyes, pesticides, explosives, and other inorganic pollutants. The catalytic studies further indicated that the activity of the catalyst correlated well with the surface area and porosity. Therefore, one can try to increase efficiency by increasing the specific surface area and porosity of the catalyst by introducing a structure directing agent.

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In the present work, a new route is demonstrated for preparing $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$ using P123 as a structure directing agent. The catalysts have excellent surface physicochemical properties. The average particle size became smaller and the pore volume became larger, and the selective adsorption of organic compounds was increased. All these factors enhanced the activity of the photocatalyst. The photocatalysts demonstrated the validity and universal applicability of P123 and could provide a new direction for the photocatalytic degradation of explosive wastewater.

2. Experimental

2.1. Sample preparation

$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$ were synthesized by the combination of sol-gel synthesis, template self-assembly, and the solvothermal treatment method. An amount of P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, $\text{EO} = \text{CH}_2\text{CH}_2\text{O}$, $\text{PO} = \text{CH}_2(\text{CH}_3)\text{CHO}$, MW 5800, Sigma-Aldrich) was dissolved in 22.5 mL pure ethanol (99.7%, Beijing Chemical Works, China) with vigorous stirring. After the complete dissolution of the P123, 15 mL tetrabutyl titanate ($\text{Ti}(\text{OBu})_4$, Sinopharm Chemical Reagent Co., Ltd., China) was added as a titanium precursor. To this solution, 12 mol/L HCl (Beijing Chemical Works, China) was added to adjust pH value to 1.00 ± 0.01 , then 0.75 g $\text{H}_3\text{PW}_{12}\text{O}_{40}$ or $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (Sinopharm) dissolved into 1 mL double distilled water was dropwise added into the mixed solution. After stirring for 2 h, another 22.5 mL ethanol was added to reduce the acidity to make hydrolysis favorable. Finally, 2 mL distilled water was added for hydrolysis (molar ratio of $\text{Ti}(\text{OBu})_4$ to distilled water was 1:4 to ensure the complete hydrolysis of $\text{Ti}(\text{OBu})_4$). The resulting acidic solution was stirred at room temperature until a gel was obtained. The gel was transferred into a hydrothermal reactor and heated to 120 °C for 2 h at a heating rate of 2 °C/min, then warmed to 150 °C for 2 h with the same rate of 2 °C/min. Subsequently, clearing, separating, drying, and milling were performed to obtain the powder. Finally, the powders were thermally treated at 400 °C for 5 h with a heating rate of 5 °C/min to remove P123. The obtained $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$ catalysts were denoted $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$, respectively. For comparison, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$ were also prepared by the same method without using P123.

2.2. Characterization

X-ray diffraction patterns were obtained with a Netherlands PaNalytical X'Pert Pro-MPD diffractometer with $\text{Cu } K_\alpha$ irradiation ($\lambda = 0.154 \text{ nm}$) operating at 40 kV and 40 mA. The structure of the samples was characterized by Raman spectroscopy using a Renishaw Invia used at 633 nm wavelength. The surface area of the composite catalysts was determined by a Nova 2200e automatic specific surface and porosity analyzer, which used the BET equation and adsorption data in the relative pressure (p/p_0) range from 0.05 to 0.3. The average pore diameter and pore volume were obtained by the BJH model at the

relative pressure of 0.976 (the catalysts were outgassed under vacuum at 200 °C overnight). The shape, size and size distribution of the catalysts were observed by scanning electron microscope (SEM, Hitachi S-4800N) with an acceleration voltage of 5 kV. The ultraviolet-visible (UV-Vis) spectra of the samples over a range of 190–600 nm were recorded with a Shimadzu UV-3600 ultraviolet-visible spectrophotometer.

2.3. Measurement of the photocatalytic activity

The photocatalytic activity of the composite catalysts was evaluated by monitoring the degradation of DNT in a suspension system. The DNT explosive wastewater was provided by an ordnance factory and contained 2,4-DNT, 2,6-DNT, and 2,3-DNT. The concentration of total nitrocompound was 400 mg/L, and the chemical oxygen demand (COD) was 3100 mg/L. The initial pH of the wastewater was 7.8. The DNT wastewater was diluted with 10 times amount of water before the process of degradation.

The reactor system consists of a xenon lamp, a set of quartz beakers, and a magnetic stirrer. The main emission wavelength range of the xenon lamp (PLS-SXE300CUV, 300 W) was 250–380 nm. The sample was irradiated with a light intensity of 100–200 mW/cm².

The photocatalytic experiments were carried out by adding an appropriate amount of catalyst (0.04 g $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ or 0.03 g $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$) into 50 mL DNT solution with the initial concentration of 40 mg/L. The pH value of the reaction solution was adjusted to 2.00 ± 0.01 by adding HClO_4 . Before irradiation, the suspension was magnetically stirred in the dark for 30 min to assure adsorption equilibrium. After different irradiation times, some wastewater was sampled from the reactor and then filtered by a microporous membrane to remove catalyst particles before analysis. The concentrations of total nitrocompounds were measured by the reducing-azo spectrophotometry method.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. XRD analysis

The phase structure of the catalysts was investigated by XRD analysis. The average crystallite sizes were determined using the Debye-Scherrer formula $D = k\lambda/\beta\cos\theta$, where k is a Scherrer constant ($k = 0.89$ for a spherical particle), λ is the wavelength of the $\text{Cu } K_\alpha$ irradiation, β is the full width at half maximum, and θ is the diffraction angle [11].

Figure 1 shows the XRD patterns of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$. All the samples showed characteristic peaks at 25.3° (101), 37.8° (004), 48.1° (200), 54.0° (105), and 62.7° (211), indicating the presence of the anatase phase. These four catalysts showed similar peaks, which suggested that the crystal structure was unchanged by the template P123 added. As shown in Table 1, the average crystal sizes of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ decreased to 15.5 and 7.8 nm, respectively.

Fig. 1. XRD patterns of samples. (1) $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$; (2) $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$; (3) $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$; (4) $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$.

Table 1

Average particle sizes of the composite catalysts.

Catalyst	Crystallite size (nm)
$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$	20.7
$\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$	13.8
$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$	15.5
$\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$	7.8

The small crystal size facilitates fast charge migration from the bulk to the surface, which leads to better catalytic activity.

3.1.2. Raman results

Raman spectra of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ were shown in Fig. 2. The peaks at 399.1, 519.5, and 640.3 cm^{-1} indicated the presence of the anatase phase [12]. According to Li et al. [13], the characteristic Raman peaks of the Keggin unit are in the range of 1100–900 cm^{-1} , where the peaks

Fig. 2. Raman spectra of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ (1) and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ (2) samples.

at 1009.5, 993.9, and 912.4 cm^{-1} corresponded to the P–O, W=O, and W–O–W bonds, respectively. For the composite $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$, the peaks corresponding to the W=O, W–O–W, and P–O bonds vibrations were broadened, and only one wide peak was observed at 1100–900 cm^{-1} . That is, there were Raman shifts due to a strong interaction between the Keggin unit and the TiO_2 network, which led to the decrease in the symmetry of either TiO_2 or $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [14]. Similar results are found with $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$. Thus the Raman results confirmed the structure integrity of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$.

3.1.3. N_2 adsorption-desorption results

The specific surface area is one of the most important properties of materials, which affects its photocatalytic activity. Figure 3 shows the N_2 adsorption-desorption isotherms and the

Fig. 3. N_2 adsorption-desorption isotherms and pore size distributions (insert) of the catalysts. (a) $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$; (b) $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$; (c) $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$; (d) $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$.

Table 2

Surface area and pore structure of the composite catalysts.

Catalyst	A_{BET} (m^2/g)	Average pore size (nm)	Pore volume (cm^3/g)
$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$	177.9	3.84	0.187
$\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$	179.3	4.36	0.199
$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$	252.2	5.69	0.378
$\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$	250.0	6.61	0.360

BJH pore size distribution of the catalysts. Table 2 lists the pore size, pore volume, and specific surface area of the samples.

The adsorption behavior is typical of mesoporous materials with capillary condensation in the mesoporous channels [15,16]. These organized pore structures are extremely useful in photocatalysis as they provide efficient transport pathways for reactant and product molecules [17,18]. The different samples display similar isotherms but have different specific surface area and pore volume. As shown in Table 2, the specific surface area and pore volume of the samples increased with the addition of the template P123. The catalyst $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ exhibited the highest specific surface area of $252.2 \text{ m}^2/\text{g}$, which was 1.42 times larger than that of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$. Similarly, the specific surface area of $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ was increased to 250.0 from $179.3 \text{ m}^2/\text{g}$.

3.1.4. SEM analysis

The SEM images shown in Fig. 4 provided visualization of the textural properties of samples and indicated that the four kinds of catalysts were made up of regular spherical particles with sizes less than 20 nm. It showed that the addition of the structure directing agent P123 did not significantly affect the particle morphology, but the particle sizes were obviously decreased, which corroborated the increase of specific surface area (Table 2).

3.1.5. UV-Vis spectra

The UV-Vis spectra of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ are shown in Figure 5.

Fig. 4. SEM images of the composite catalysts. (a) $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$; (b) $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$; (c) $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$; (d) $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$.

Fig. 5. UV-Vis absorption spectra of the samples.

The composite catalysts exhibited broad and strong absorption in the range from 200 to 400 nm, and the adsorption bands showed an obvious red shift compared with pure TiO_2 . The results indicated that the charge transfer band was shifted to a higher wavelength and the band gap of the composite materials became narrower after the introduction of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$.

The absorption spectrum of pure TiO_2 was from the charge transfer from the O $2p$ to Ti $3d$ orbitals. However, the charge transfer from O $2p$ to a new orbital constructed from the hybridization of Ti $3d$ and W $5d$ orbitals contributed to the absorption spectra of the composite catalysts [14,19]. This is the most important factor in the narrowing of the band gap of the composites. Therefore, the Keggin unit can efficiently improve the electronic properties of TiO_2 in the composites.

3.2. Photocatalytic degradation of DNT by the composite catalysts

3.2.1. Effect of P123 dosage

Figure 6 illustrates the degradation rate of DNT by photocatalytic degradation using $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ as the catalyst.

As shown in Fig. 6(a), the organic compounds were effectively degraded. The total degradation rate of DNT was as high as 95% after 4 h of irradiation under the optimum conditions. In order to determine the optimum dosage of P123, different dosage of P123 were added in the preparation of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$. The results (Fig. 6(b)) clearly indicated that the degradation rate obviously increased with increasing P123 amount from 0.5 to 2.0 g, but only slightly changed with the use of 2.0 to 5.0 g, which meant that the optimum dosage of P123 was 2.0 g for $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$.

Figure 7 compares the degradation rate of DNT over $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ catalyst. It shows that although DNT was effectively degraded with all the catalysts, the degradation rate was obviously higher when the amount of P123 used was 1.0 g, which means the optimum dosage of P123 for $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$ was 1.0 g.

As mentioned above, the optimum addition amount of P123 for $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$ were 2.0 and 1.0 g, respectively, which was most beneficial for increasing the spe-

Fig. 6. Photocatalytic degradation of DNT by $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ with different P123 dosages. Reaction conditions: DNT 40 mg/L, initial pH 2.0, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ loading 20%, catalyst dosage 0.8 g/L, reaction time 240 min (b).

Fig. 7. Photocatalytic degradation of DNT by $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ with different P123 dosages. Reaction conditions: DNT 40 mg/L, initial pH 2.0, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ loading 20%, catalyst dosage 0.6 g/L, reaction time 240 min (b).

cific surface area and improving the pore structure of the composites.

3.2.2. Kinetics of the photocatalytic degradation of DNT

Photolysis and photocatalytic degradation processes are often modeled as first order kinetics [20]. Hence, the degradation kinetics of DNT was fitted using the first order kinetics model $\ln C_0/C_t = kt$, where k is the reaction rate constant ($\text{mg}/(\text{L}\cdot\text{min})$), t is the illumination time (min), C_0 is the initial DNT concentration (mg/L), and C_t is the DNT concentration at irradiation time t (mg/L).

The photocatalytic activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ is compared in Fig. 8. The photocatalytic activity of commercial Degussa P25 was also investigated for comparison. The rate constants and reaction half-time of the different catalysts are given in Table 3.

The experimental data were fitted well with the formula, showing that DNT photocatalytic degradation follows first order kinetics. The data indicate that 39% DNT was removed after 4 h of irradiation without a catalyst, indicating some direct photolysis occurred under UV light. However, the conversion of DNT is considerably increased with a catalyst. The results showed that all the composite catalysts exhibited significantly higher photocatalytic activity than commercial Degussa

P25. The rate constant reaches $0.0094 \text{ mg}/(\text{L}\cdot\text{min})$ over $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ catalyst, 1.8 times higher than $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$, and the reaction half time was decreased from 2.2 to 1.2 h. Compared with $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ displayed much higher photocatalytic activity with the

Fig. 8. Comparison of removal efficiency with different catalysts. (1) No catalyst; (2) Degussa P25; (3) $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$; (4) $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$; (5) $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$; (6) $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$. Reaction conditions: DNT 40 mg/L, initial pH 2.0, catalyst dosage 0.6 g/L (3 and 5) and 0.8 g/L (2, 4, and 6), $\text{H}_3\text{PW}_{12}\text{O}_{40}$ loading 20%, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ loading 20%.

Table 3

First order kinetics parameters for DNT degradation by the different catalysts.

Catalyst	$k/(\text{mg}/(\text{L}\cdot\text{min}))$	$t_{1/2}/\text{h}$	R^2
No catalyst	0.0021	5.5	0.9944
Degussa P25	0.0043	2.7	0.9931
$\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$	0.0053	2.2	0.9993
$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$	0.0065	1.8	0.9994
$\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$	0.0094	1.2	0.9981
$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$	0.0125	0.9	0.9966

degradation rate of DNT reaching 95% after 4 h irradiation. The reaction rate constant of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ was 1.9 times higher than that of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$, and the reaction half time was almost reduced to half.

These results illustrated that the rate constants for the degradation of DNT were made significantly higher by the adding of a suitable amount of template. The excellent catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ was attributed to their smaller crystal size and higher surface area. The small crystal size facilitated fast charge migration from the bulk to the surface, and the large surface area provided more active sites for heterogeneous photocatalysis, which gave higher photocatalytic activity [21–23]. In addition, with the directing function of P123 in the aqueous solution, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ exhibited a dual function for the degradation of the organics [24,25]. Their mesoporous structures led to a faster internal diffusion rate than in $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$, which is advantageous for the separation of the electron and hole [26].

Therefore, it was concluded that the photocatalyst activity depends on both the specific surface area and the particle pore structure. The structure directing agent P123 plays an important role in the preparing of mesoporous $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$.

3.2.3. Recyclability of the catalyst

$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ was chosen to evaluate the stability and reusability of the composite. This is important from the view of industrial application. The catalyst was separated, washed, and dried after the reaction and was used for the next run. The catalytic reaction was repeated three times.

As shown in Fig. 9, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ maintained its activity after it was reused three times, suggesting that the composite catalyst exhibited high stability. Therefore, the new route that combines sol-gel synthesis, template self-assembly, and a solvothermal treatment is suitable for preparing high stable photocatalyst.

4. Conclusions

A new route using the combination of sol-gel synthesis and solvothermal treatment was demonstrated for preparing four kinds of composite catalysts. The structure directing agent P123 plays an important role in preparing mesoporous $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$, which possessed higher specific surface area, and smaller crystal size. Photocatalytic

Fig. 9. Recycled runs in the photocatalytic degradation of DNT using $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ as the photocatalyst. Reaction conditions: DNT 40 mg/L, initial pH 2.0, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ loading 20%, catalyst dosage 0.8 g/L.

tests showed that $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ exhibited higher photocatalytic activities for DNT degradation. Using $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2(\text{P})$ as the catalyst, the degradation rate of DNT reached 95% after 4 h of irradiation and maintained after three cycles.

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Graphical Abstract

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Photocatalysis of dinitrotoluene decomposition by $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$ prepared by a modified sol-gel synthesis and solvothermal treatment method

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This article focuses on the preparation of new materials (POMs/ TiO_2) using P123 as a structure directing agent with solvothermal treatment. Photocatalytic tests show that new materials exhibit high photocatalytic activity for DNT degradation.

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采用溶胶-凝胶-溶剂热路径合成 $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ 和 $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$ 及其光催化降解二硝基甲苯

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摘要: 以非离子表面活性剂P123为结构导向剂, 采用溶胶-凝胶与溶解热相结合方法, 制备了两类介孔材料 $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ 和 $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$, 并对其进行了表征. X射线粉末衍射和拉曼光谱分析表明, 所制催化剂为锐钛矿晶型, 体系中 $\text{H}_3\text{PW}_{12}\text{O}_{40}$ 和 $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ 的Keggin结构经400 °C焙烧后仍保持完整. $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ 和 $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$ 的平均粒径分别为15.49和7.75 nm. N_2 吸附-脱附和扫描电镜结果表明, P123的加入使催化剂的粒径减小, 比表面积和孔体积明显增大, 其中 $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ 和 $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$ 的比表面积分别高达252.2和250.0 m²/g. 紫外漫反射吸收光谱表明, 与纯 TiO_2 相比, 复合催化剂的吸收光谱发生了明显的红移, 且吸收强度明显增大. 催化剂对DNT降解实验表明, 在最佳操作条件下降解率可高达95%.

关键词: 介孔材料; 多金属氧酸盐; 二氧化钛; 结构导向剂; 二硝基甲苯; 光催化降解

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