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ORIGINAL CONTRIBUTION

Effect of PEG with different M_W as template direction reagent on preparation of porous TiO_2/SiO_2 with assistance of supercritical CO_2

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Abstract Titania–silica composite have been prepared using polyethylene glycol (PEG) with different molecular weights (M_w), PEG20000, PEG10000, and PEG2000, as template in supercritical carbon dioxide (SC CO_2). The composite precursors were dissolved in SC CO_2 and impregnated into PEG templates using SC CO_2 as swelling agent and carrier. After removing the template by calcination at suitable temperature, the titania–silica composite were obtained. The composite were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, and nitrogen sorption–desorption experiment. Photocatalytic activity of the samples has been investigated by photodegradation of methyl orange. Results indicate that there are many Si–O–Ti linkages in the TiO_2/SiO_2 composite; the PEG template has a significant influence on the structure of TiO_2/SiO_2. In addition, the TiO_2/SiO_2 prepared with PEG10000 exhibited high photocatalytic efficiency. So this work supplies a clue to control and obtain the TiO_2/SiO_2 composite with different photocatalytic reactivity with the aid of suitable PEG template in supercritical CO_2.

Keywords PEG · Template · TiO_2/SiO_2 · Supercritical CO_2 · Photocatalysis

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Introduction

Titanium dioxide or titania is one of the most utilized particulate materials in the world. It is commercialized as the most powerful photocatalyst because it has high photoactivity for most photocatalysis reactions such as purification of water [1, 2] or air [3], and is inexpensive as well as nontoxic to human life. The addition of silica in titania not only enhances the thermal stability for the phase transformation of titania particles from anatase to rutile [4] but also increases the surface area [5] and surface acidity [6]. It is proven as an efficient way to improve the activity of a photocatalyst. Now, titania–silica-mixed oxides have attracted considerable attention due to their application as glasses with a low thermal coefficient [7], heterogeneous catalyst to degrade the organic molecules [8–11], and catalyst support [12–17]. The conventional preparation method for titania–silica includes precipitation method, microemulsion method, sol–gel method, hydrothermal process, and so on [18]. However, massive organic solvents are needed in these processes, and this does detriment to the environment. Therefore, searching for a new solvent that is beneficial to the environment becomes the current research hotspot. Supercritical carbon dioxide becomes the ideal choice [19, 20] because of its excellent physical chemistry properties and its advantages such as non-toxic, stable, low-cost, and so on.

Template synthesis method has been playing an important role in the fabrication of nanocrystalline oxides with various surface and crystalline properties. Especially, polymer has been acknowledged as a crucial template for the preparation of materials with novel properties and morphologies [21–23]. With these polymer templates, siliceous oxide is the principal product, although some nonsiliceous oxides, oxides of Pd, Ti, W, Mo, Hf, Zr, and

Nb, have been synthesized [24–33]. The polymer templates can exhibit very complex phase behavior in an aqueous solution and has been expected to form new products with varied structure, together with improving the properties of known materials [34]. Among all the used polymer templates, PEG is very popular, and it has been reported that it could lead to the formation of nanocrystals with high performance [35–37]. PEG is a nondegradable, hydrophilic polymer that can be cross-linked into hydrogels through various chemistry methods. PEG-based hydrogels were developed by introducing terminal acrylate functional groups that could take part in photopolymerization reactions [38–40]. In this process, the surfactant PEG serves two essential functions: (a) as a structure-directing reagent and (b) as a coordinating ligand to lower the reactivity of the tetrabutyl titanate (TBTT) [41]. In our previous study, we have used PEG20000 as template to prepare the composite TiO_2/SiO_2 that existed in a spheric form or a cubic form inserted with many holes [42]. We demonstrated that the microstructure and macroproperty of TiO_2/SiO_2 composite depend strongly on the experimental pressure during the impregnation process in SC CO_2. And it indicated that, with the aid of suitable polymer templates in supercritical CO_2, the special micrography of TiO_2/SiO_2 composites can be controlled.

In this study, in order to further study the effect of PEG template on the nanoporous structure of TiO_2/SiO_2, we use PEG of different M_w as template direction agent to prepare the titania–silica mesoporous composite and investigate their difference on the properties of products. The product was characterized by Fourier transform infrared (FT-IR), X-ray diffraction (XRD), and nitrogen sorption–desorption experiment. FT-IR results can confirm the formation of the Ti–O–Si heterolinkages in the TiO_2/SiO_2 composites product. From XRD, it indicates that the titanium dioxide is in anatase phase. Nitrogen sorption–desorption experimental results indicate that the optimal experimental condition is 60 °C, 22 MPa, and PEG10000. In addition, we study the photocatalytic activity of the products by photodegrading the methyl orange. The detection results displayed that the TiO_2/SiO_2 prepared with PEG10000 exhibited high photocatalytic efficiency in the degradation of methyl orange.

Materials and methods

Materials

TBTT and tetraethyl orthosilicate (TEOS), both of which were offered by China Medicine Group Shanghai Chemical Reagent Company, were used as titania source and silica source. Polyethylene glycol (PEG20000) was supplied by Tianjin Tiantai Fine Chemical Incorporated Company. Polyethylene glycol (PEG10000) was supplied by China Medicine Group Shanghai Chemical Reagent Company. Polyethylene glycol (PEG2000) was offered by Guangdong Shantou Xilong Chemical Plant. CO_2 with purity of 99.9% was provided by Zhengzhou Gas Company and used as received. Aqueous ammonia ($NH_3{\cdot}H_2O$) was purchased from Luoyang Henghui Fine Chemical Reagent Company and used as received. Anhydrous ethanol (C_2H_5OH) was offered by Anhui Ante biochemical Company, Ltd. Methyl orange dye (the third reagent plant in Shanghai) were of reagent grade and were used without any further purification.

Impregnating process in supercritical CO_2

In a typical experiment, 2 mL of TBTT and 2 mL of TEOS were placed into the bottom of a stainless steel autoclave (Hai'an High Pressure Autoclave Factory, China) of 50 mL capacity, and their mass ratio is 1:0.94. A 0.500-g polyethylene glycol was placed in a stainless steel cage fixed at the upper part of the autoclave so that it does not contact with the precursors mixture solution. The autoclave temperature was adjusted up to the desired experimental value, and CO_2 was filled into the autoclave by a syringe pump (DB-80, Beijing Satellite Manufacturing Factory) until the desired pressure was obtained, and the supercritical condition was kept for 8 h. Then CO_2 was released by venting, and the PEG, which impregnated with the precursors was taken out.

Thermal treatments

After cooling to room temperature, the product was heated at 35 °C for 12 h in vacuum.

Hydrolysis

The product hydrolyzed in the pre-mixed water solution that contains ammonia and anhydrous ethanol with the assistance of ultrasonic apparatus (KQ-100E Kunshan Ultrasonic Apparatus Corporation); the volume ratio of $NH_3{\cdot}H_2O/C_2H_5OH$ is 1:10.

Calcination

Before calcination, the hydrolyzed product was washed, filtrated, and heated at 35 °C for 6 h in vacuum, then it was calcinated at 600 °C in air flow to remove the template.

Characterization

The calcinated products were characterized with nitrogen adsorption–desorption experiment, and the isotherms at

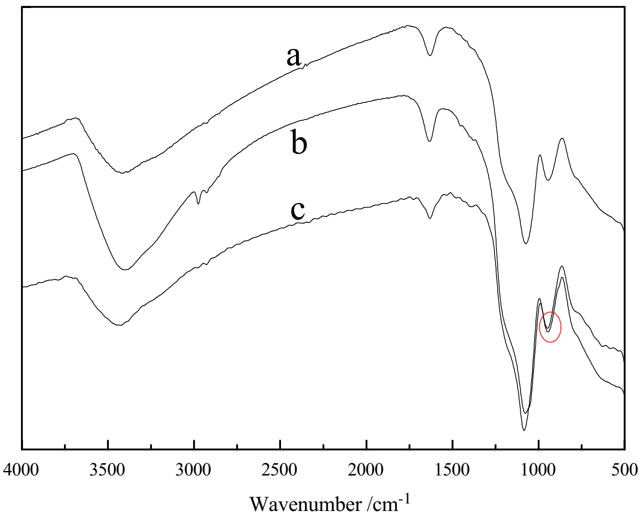


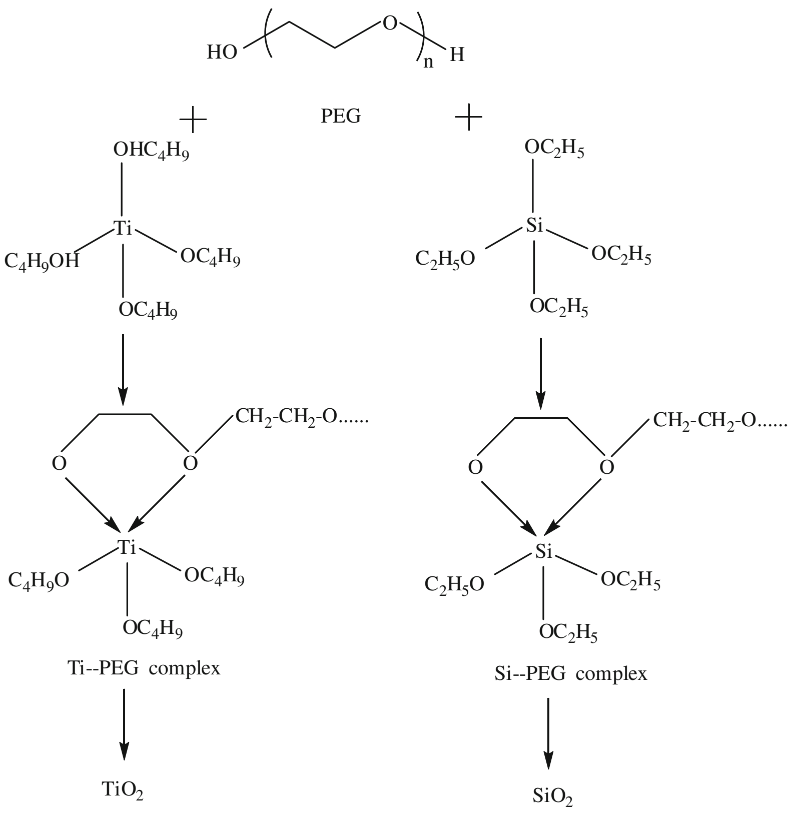
Fig. 1 FT-IR spectra of TiO_2/SiO_2 composite prepared at 60 °C and 22 MPa for 8 h with different M_w PEG as template in supercritical CO_2. (**a** PEG2000, **b** PEG10000, and **c** PEG 20000)

77 K were collected on a Quantachrome NOVA 1,000-e surface area and pore size analyzer. Before this measurement, the calcinated products were heated at 473 K in 10^{-6} Torr nitrogen for 1.5 h. The Barret–Joyner–Hallender (BJH) method was used to calculate the pore size distribution. X-ray diffraction data were recorded on a Rigaku D/Max-3B using Cu Kα radiation at a scanning speed of 6°/min in the range of 10–80°. IR spectra were received using a Bruker FT-IR tensor 27 spectrophotometer by employing KBr pellet technique.

Photocatalytic activity measurements

Photocatalytic activities of the samples have been evaluated by decomposition of methyl orange in a continuous reactor. A 500-W high pressure Xe lamp has been used. Lamp chamber is surrounded by circulating water to maintain reaction at room temperature during the process of

Scheme 1 Hydrolysis mechanism of the precursors with the help of PEG template



hydrolysis reaction:

$$Ti(OC_4H_9)_4 + nH_2O \longrightarrow Ti(OC_4H_9)_{4-n}(OH)_n + nC_4H_9OH$$

$$Si(OC_2H_5)_4 + nH_2O \longrightarrow Si(OC_2H_5)_{4-n}(OH)_n + nC_2H_5OH \quad (n=1,2,3,4)$$

polymerization reaction:

$$Ti(OC_4H_9)_3\text{-}OH + OH\text{-}Ti(OC_4H_9)_3 \longrightarrow Ti(OC_4H_9)_3\text{-}OTi(OC_4H_9)_3 + H_2O$$

$$Si(OC_2H_5)_3\text{-}OH + HO\text{-}Si(OC_2H_5)_3 \longrightarrow Si(OC_2H_5)_3\text{-}O\text{-}Si(OC_2H_5)_3 + H_2O$$

$$Ti(OC_4H_9)_3\text{-}OH + HO\text{-}Si(OC_2H_5)_3 \longrightarrow Ti(OC_4H_9)_3\text{-}O\text{-}Si(OC_2H_5)_3 + H_2O$$

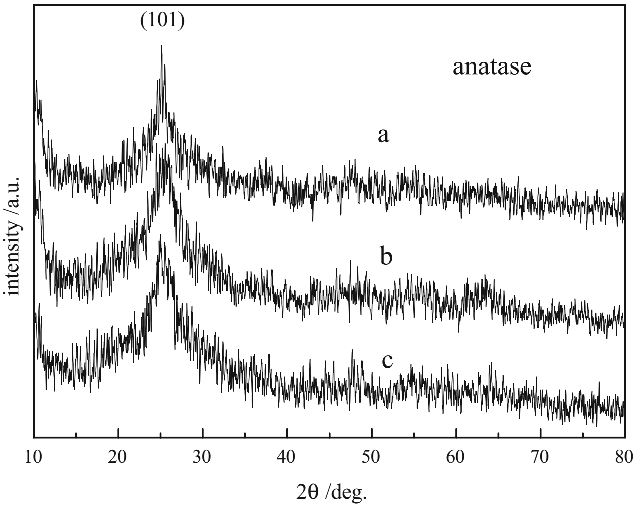


Fig. 2 Wide-angled XRD patterns of TiO_2/SiO_2 prepared with different M_w PEG (**a** PEG2000, **b** PEG10000, and **c** PEG20000) as template at 60 °C and 22 MPa for 8 h in SC CO_2, and calcined at 600 °C for 8 h

experiment. Two hundred and fifty milliliters of 20 ppm methyl orange solution was mixed with the catalysts, stirred, and aerated throughout the experiment. Then, the Xe lamp was switched on to start photodegradion of methyl orange dye. After definite irradiation times, suitable volumes of solution was analyzed by UV–vis absorbency on Shimadzu UV–Vis 2401PC spectrophotometer to measure the remaining dye concentration.

Results and discussion

Figure 1 shows the FT-IR spectra of the TiO_2/SiO_2 prepared with different M_W PEG [(a) PEG 2000, (b) PEG 10000, and (c) PEG 20000) as template in supercritical CO_2. A distinct and strong peak at 1,085 cm^{-1} that assigned to the asymmetrical vibration of the Si–O–Si bond in the tetrahedral SiO_4 unit of the SiO_2 matrix [43, 44] can be observed. The peak at 2,968.95 cm^{-1} attribute to the stretching vibration of the –C–H– bond. The symmetrical Si–O–Si stretching vibration appeared at 795 cm^{-1}, along with an absorption peak at 954 cm^{-1}, has been ascribed to the vibration involving a SiO_4 tetrahedron bonded to a titanium atom through Si–O–Ti bonds [44–46]. The presence of this band confirms the presence of Si–O–Ti linkages in the TiO_2/SiO_2 composite product. Moreover, the Si–O–Si bond at 1,085 $cm^{-1}$and Si–O–Ti bond at 954 cm^{-1} in TiO_2/SiO_2 prepared with PEG 2000 are less intense compared to that of TiO_2/SiO_2 prepared with PEG20000 or PEG10000. This is due to the interaction between the aether groups and the metal ion, the mechanism is shown in the Scheme 1. The addition of PEG lowers the reactivity of the TBTT in the hydrolysis process. A mass of aether groups exist in the structure of PEG. The higher the M_W of PEG is, the more slowly the precursor TBTT hydrolyzed. Then, a less amount of Ti–O–Ti bonds formed in the hydrolyzed process and the probability of forming Si–O–Ti bond is much higher than that prepared with lower M_W at the same condition.

Figure 2 shows the XRD result of the calcinated TiO_2/SiO_2 products. These patterns indicate the amorphous nature of the composite oxides together with the presence of anatase. The major peak appears at 25.3°, corresponding to the tetragonal phase of titania anatase. No characteristic peak of silica occurs that indicates the phase of the silica is amorphous. The peak at 25.3° is broad, indicating that the average crystallization size was relatively small. The results above are in accordance with the data we obtained from the nitrogen adsorption–desorption isotherms and BJH pore radius distributions of TiO_2/SiO_2.

In order to study the effect of different M_W PEG on the experiment results and investigate the cooperation effect of precursors TEOS and TBTT on the product, we prepared pure SiO_2 and TiO_2/SiO_2 product, respectively. Tables 1 and 2 show the detailed data of BET surface area of different samples that were prepared at different experimental conditions. The calcinated products SiO_2 were prepared with different M_W of PEG in SC CO_2 at 22 MPa, and 50 and 60 °C followed by calcinations. The products TiO_2/SiO_2 were prepared at 22 MPa and at the temperature range from 50 to 70 °C followed by calcinations. From Table 1, it can be seen that the BET surface area and total pore volume both increase with the increasing of PEG M_W. The results can attribute to the different steric hindrance of PEG with different M_W. Compared with PEG2000 and PEG10000, the steric hindrance of PEG

Table 1 BET surface area, total pore volume, and pore diameter of calcinated products SiO_2 synthesized with PEG

Temperature (°C)	Pressure (MPa)	PEG (M_w)	Total pore volume (cc/g)	Average pore radius (nm)	BET surface area (m^2/g)
50	22	2,000	0.0608	4.4042	27.59
		10,000	0.0897	5.1378	29.04
		20,000	0.0935	4.5352	41.25
60	22	2,000	0.0289	3.0564	18.88
		10,000	0.0852	6.7991	25.06
		20,000	0.4420	5.1848	170.50

Table 2 BET surface area, total pore volume, and pore diameter of calcinated products TiO_2/SiO_2 synthesized with PEG

Temperature (°C)	Pressure (MPa)	PEG (M_w)	Total pore volume (cc/g)	Average pore radius (nm)	BET surface area (m^2/g)
50	22	2000	0.1504	2.0957	143.51
		10,000	0.3507	5.1301	136.72
		20,000	0.2123	3.6873	115.16
60	22	2,000	0.2027	2.6519	152.86
		10,000	0.4075	4.2568	191.44
		20,000	0.1769	3.1705	111.34
70	22	2,000	0.1373	2.4622	111.49
		10,000	0.4107	5.1903	158.24
		20,000	0.2961	4.9608	119.39

20000 is the largest. The large steric hindrance can help to impede the aggregation of hydrolyzed particles, and the product of well-porous structure can be obtained. So, the BET surface area and total pore volume of the product prepared with high M_w PEG are comparatively larger.

From Table 2, we can see that nearly all the average pore radius, BET surface area, and total pore volume of the TiO_2/SiO_2 vary in negative *V* with the increasing M_W of PEG at the same experimental conditions, and the BET surface area can be up to 191.44 m^2/g at 60 °C, when PEG10000 was used as the template. In this preparation process, the surfactant PEG template serves two essential functions: (a) as a structure-directing reagent and (b) as a coordinating ligand to lower the reactivity of the TBTT [41]. For the composite precursor system, there is apparent difference with the pure SiO_2 precursor system, i.e., the BET surface area of the product does not increase monotonously with PEG molecular weight, and these is a maximum point with PEG10000 as template. It can be suggested that the steric hindrance of PEG loses its significant effect on the size and the size distribution of particles when it is up to a certain degree in the composite precursor system. And the cooperation effect of the precursors TEOS and TBTT leads to a maximum BET surface area of TiO_2/SiO_2 composite product prepared with PEG10000 template. The detail mechanism needs to be further studied. In addition, the SC CO_2 exerts its unique effect in the preparation process. For supercritical fluid, its solvent effect can be adjusted with experimental pressure [47, 48], and it helps to realize the beneficent reaction among the precursor mixture, PEG template, and SC CO_2. In the system, all the following factors such as (a) solubility of precursors in the SC CO_2, (b) swelling and plasticization of PEG template induced by SC CO_2, and (c) the molecular interaction of PEG as chelation reagent with precursor mixture, should match each other. So, it can be concluded from our study that for the mixed precursors of TBTT and TEOS to prepare TiO_2/SiO_2 composite, the optimal template is PEG10000.

The nitrogen adsorption–desorption isotherms and BJH pore radius distributions of the TiO_2/SiO_2 composite are shown in Fig. 3. Samples were heated at 473 K in 10^{-6} Torr

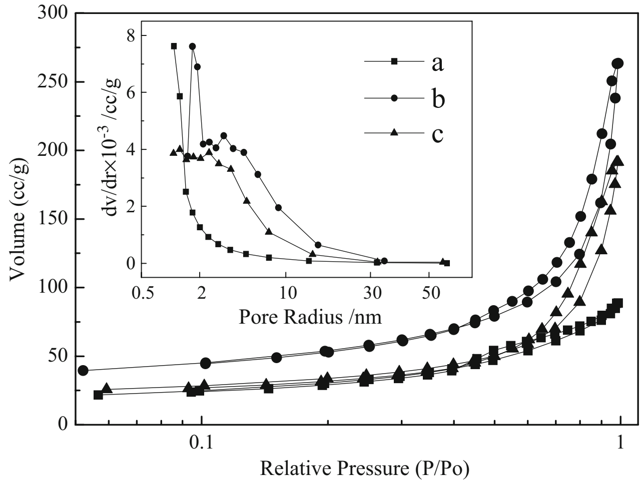


Fig. 3 Nitrogen adsorption–desorption isotherms and BJH pore radius distributions of TiO_2/SiO_2 synthesized at 60 °C and 22 MPa with different M_w PEG (**a** PEG2000, **b** PEG10000, and **c** PEG 20000) as template in SC CO_2

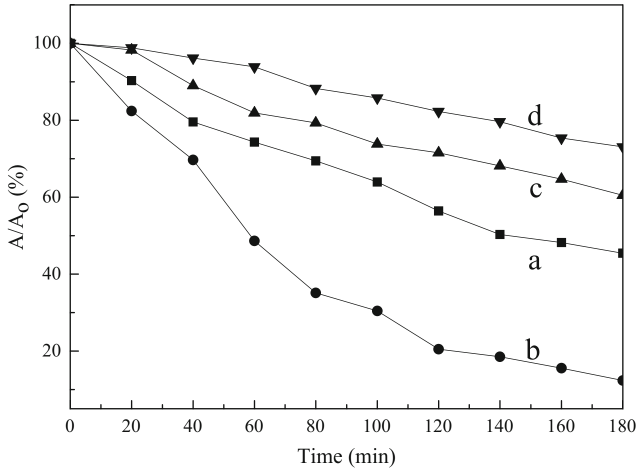


Fig. 4 Evaluation of the photocatalytic of TiO_2/SiO_2 synthesized at 60 °C and 22 MPa with different Mw PEG (**a** PEG2000, **b** PEG10000, and **c** PEG20000) as template in SC CO_2 and the concentration variation of the pure methyl orange (**d**) with the irradiation of Xe light of 500 W

nitrogen for 1.5 h before this measurement. Both the material prepared with PEG10000 and PEG20000 give typical irreversible type II sorption isotherms with a hysteresis loop that account for the filling of mesopores. The first adsorption step is accounted for by a monolayer adsorption of N_2 on the pore walls, which is followed by a sudden increase occurring at $P/P_0>0.7$. The increase suggests a large pore volume, and the sharpness of these steps reveals the uniformity of the mesopore size distribution. This attributes to the low viscosity and high diffusivity of SC CO_2, the impregnated precursors can be introduced into the pores of PEG template deeply. But the isotherm of the material prepared with PEG2000 is in a line, and it corresponds to the Freundlich adsorption. Pore size distribution of titania/silica composite calculated by BJH method from nitrogen sorption isotherm is shown in the inset of Fig. 3. It can be seen that the pore diameter of the particles prepared with PEG20000 and PEG10000 are around 5 nm in diameter and that prepared with PEG 2000 is around 2 nm in diameter.

Because BET surface area of the samples TiO_2/SiO_2 prepared with PEG10000 are higher than that prepared with PEG2000 and PEG20000 at 60 °C and 22 MPa, so a higher photocatalytic activity is expected among the three products. The photocatalytic activity of the TiO_2/SiO_2 and the concentration variation of the pure methyl orange were evaluated based on the decomposition of methyl orange with the irradiation of Xe light of 500 W. The reduction of methyl orange absorption maximum at 460 nm was taken as indication of the photocatalytic reactivity of TiO_2/SiO_2. Figure 4 shows the degradation curves for the TiO_2/SiO_2 prepared at 60 °C and 22 MPa with PEG2000, PEG10000, and PEG20000 template. The decrease rate in the methyl orange with TiO_2/SiO_2 prepared with PEG10000 is considerably faster compared to that prepared with PEG20000 and PEG2000, and in pure methyl orange. The higher efficiency is contributed to its high BET surface area and porosity. Furthermore, the presence of its highly photoactive anatase nanocrystalline structure and light transmittance also plays a certain role in the degradation process. The results can be confirmed with the experimental data of the nitrogen adsorption–desorption, and it demonstrated that the PEG template has a profound effect on the photocatalytic activity simultaneously.

Conclusion

In this article, we studied the effect of the different molecular weight of template PEG on the structure of titania/silica composites in the SC CO_2 assisting process. It is found that the PEG template with different M_w plays a significant role on the preparation process. Nitrogen sorption experimental result indicates that PEG template has preferable direction effect for the precursor mixture. The BET surface area and total pore volume of pure SiO_2 increase with the increasing of the PEG M_w. It also showed that nearly all the BET surface area and total pore volume of TiO_2/SiO_2 display a maximum point with an increase of the PEG M_w at the same experimental conditions. Compared with PEG2000 and PEG20000, the BET surface area of TiO_2/SiO_2 prepared with PEG10000 can be up to 191.44 m^2/g at 60 °C and the activity also is the maximum. Moreover, it demonstrated that template polymer has an important influence on the photocatalytic reactivity of the product. So this work can open a gateway to control and obtain the TiO_2/SiO_2 composite with high BET area and high photocatalytic reactivity with the aid of suitable polymer template in supercritical CO_2.

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