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Investigation of Photocatalytic Activity of TiO_2/SiO_2 Nanocomposite in Presence of Carboxy Methyl Cellulose, Poly(vinyl pyrrolidone) and Hydroxyl Propyl Cellulose

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TiO_2/SiO_2 nanocomposites powder are the most important materials due to their extensive application in the field of photocatalysis, were prepared by the sol-gel method with and without poly(vinyl pyrrolidone), carboxy methyl cellulose and hydroxyl propyl cellulose as additives. In this work, the influence of these additives on the properties, structure and photocatalytic activity under UV-irradiation for removal of organic pollutant were investigated by IR spectra, scanning electron microscopy, energy dispersive analytical X-ray and X-ray diffraction methods. The results suggest that these additives play an important role in decreasing of particles size and TiO_2/SiO_2 with hydroxy propyl cellulose was the best sample.

Key Words: Sol-gel, Nanocomposite, Photocatalytic activity.

INTRODUCTION

It has been revealed that, in the last decade, TiO_2 to be the best candidate for photocatalytic applications[1-3]. Nano-sized TiO_2 particles have a relatively large surface area per unit mass and volume; therefore, these particles show high photocatalytic activity, which facilitates the diffusion of the surface, generated charge carriers under light irradiation[4,5]. Basically, the photocatalytic process is initiated by the photogeneration of hole/electron pairs in the semiconductor by absorption of UV-light with energy equal to or higher than the corresponding band gap for TiO_2 anatase $E_g = 3.2$ eV[6]. The organic substances that come into contact with the surface decompose due to the photocatalysis property of TiO_2 consequently prevent them from building up[7].

In recent years, numerous studies have shown that TiO_2-SiO_2 composites exhibit an enhanced photocatalytic activity, which makes TiO_2-SiO_2 composites particularly attractive for catalytic applications[8,9-18]. In addition to granular interface effects, other physico-chemical and structural properties can also influence wet ability properties of TiO_2-SiO_2 composite particles. Especially, morphological properties (surface roughness, open porosity) are very important aspect to consider[19].

In this work, we have chosen a sol-gel method to prepare TiO_2 photocatalysts. Since particle size is an important parameter for photocatalysis[20-33], we have investigated the effects of carboxy methyl cellulose (CMC), poly(vinyl pyrrolidone) (PVP) and hydroxyl propyl cellulose (HPC) as modifiers for the size of TiO_2-SiO_2 particles and for choosing the best additive for photocatalytic activity. The advantages of the sol-gel technique are molecular-scale mixing of the components, high purity of precursor and homogeneity of sol-gel products with high isotropy of physical, morphological and chemical properties[34].

EXPERIMENTAL

Titanium tetra isopropoxide (AR analytical grade, Merck Chemical Company) were used as titanium sources for the preparation of the TiO_2 phtocatalysts. Carboxy methyl cellulose (CMC), poly(vinyl pyrrolidone) (PVP) and hydroxyl propyl cellulose (HPC), HNO_3, SiO_2 colloid solution and absolute ethanol and deionized water were purchased from Merck Chemical Company.

Preparation of samples: Four samples of TiO_2/SiO_2 photocatalyst were prepared by using the sol-gel method. Titanium tetra isopropoxide was dissolved in absolute ethanol (with molar ratio titanium tetra isopropoxide/ethanol = 1/75) then additive was added and stirring until complete dissolution to this base solution (Table-1). Then, another mixture of absolute ethanol, HNO_3, deionized water and SiO_2 (with molar ratio ethanol/HNO_3/H_2O/SiO_2 = 43/0.2/1/30) was added dropwise under vigorous stirring at room temperature. The obtained transparent colloidal suspension was stirred (45 min), then kept for 48 h to allow it be formed as a gel. The sample was dried in air and treated at 500 ºC for 2 h.

TABLE-1
FORMULATION OF SAMPLES

Sample	Amount of CMC in solution g/g_{sol}	Amount of PVP in solution g/g_{sol}	Amount of HPC in solution g/g_{sol}
1	–	–	–
2	4.5×10^{-3}	–	–
3	–	4.5×10^{-3}	–
4	–	–	4.5×10^{-3}

Photocatalysis: The solution of methyl orange (5 mg L^{-1}) in deionized water was selected as a pollutant solution for photodegradation. This solution was set in the vicinity of nano photocatalist powder (0.5 g powder in 1 L solution) and then was kept for 24 h in the darkness, in order to eliminating the absorption effect of the solution in the catalyst. Finally it was placed under a 15 W UV lamp (Osram). The changes of methyl orange was recorded by an UV spectrometer model Varian.

Set up of photocatalytic reactor: The photoreactor system which is shown in Fig. 1 was chosen for photocatalytic reduction studies of pollutant solution. This photoreactor system consisted of a cubic borosilicate glass reactor vessel with an effective volume of 1000 mL, a cooling water jacket and a 15W UV lamp with a quartz cover positioned inside the solution, as an UV light source was used. The reaction temperature was maintained at 25 ºC using cooling water.

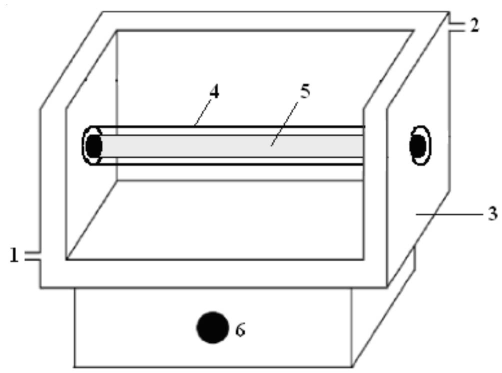

Fig. 1. Schematic diagram of the photoreactor system: 1-Water entrance, 2-water exit, 3-glass jacket, 4-quartz cover, 5-UV lamp, 6-stirrer

XRD measurements were performed using a Philips x' pert pero MPD diffractometer with CuK_α radiation from 10-80 (2θ) at room temperature. FT-IR spectra were obtained as KBr pellets in the range of 4000-500 cm^{-1} using Shimadzu FT-IR spectrophotometer. Morphology and microanalysis of the samples was observed by a scanning electron microscope (SEM, SEM-4100, Jeol). Ultraviolet-visible (UV-VIS) absorption spectrum was obtained by means of Varian UV-VIS spectrometer.

RESULTS AND DISCUSSION

Effect of additives on the microstructure: FT-IR spectra of the TiO_2/SiO_2 powders, with and without additives were represented in Fig. 2. The wide absorptions band around 3700-3100 cm^{-1}, which can be attributed to the OH stretching vibration of surface hydroxyl group[35-37]. A great amount of propanol appears during the hydrolysis of titanium tetra isopropoxide, which leads to the appearance of hydroxyl bands (3700-3100 cm^{-1}). The intensity of bands in samples 1, 2 and 3, decrease

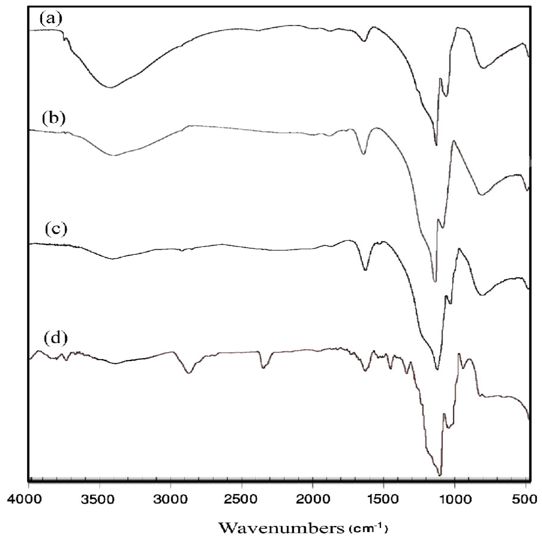

Fig. 2. FT-IR spectra of the sample sols. (a) sample 1, (b) sample 2, (c) sample 3, (d) sample

in sample 4, because the association of hydroxyl is restrained by the steric effect of hydroxyl[36]. The absorption band around 1635 cm^{-1} was stretching mode of physically adsorbed water and hydroxyl group[35,36,38].

The bands at 1117 cm^{-1} in samples 1, 2, 3 and 4 can be assigned to asymmetric stretching vibration of the Ti-O bands[36,39] and the bands at 1073 cm^{-1} in samples 3 and 4 are the asymmetrical vibration of the Si-O-Si bands[40]. The peak at 602 cm^{-1} can be assigned to symmetric stretching vibration of the Ti-O-Ti group[36,38] and 1037 cm^{-1} which may correspond to Ti-O-C bending[38]. The Ti-O-C may result from the interaction between the Ti-O network and the organic polymers (CMC, PVP or HPC).

SEM picture of sample 1 without any additive, contains high agglomeration and it has the most range particle distribution and largest size and it is scattered. Uniformity in sample 2 is better than sample 1, but worse than the others. When PVP was added, TiO_2/SiO_2 particle size decreases and particle distribution becomes narrow with a monotonously in particle size. Sample 4 which contains HPC has the most uniform particle distribution with low agglomeration in comparison with others.

Effect of CMC, PVP and HPC on the anatase phase: XRD patterns of all samples have been shown in Fig. 3. As it is observed, in XRD pattern of sample 1, without any additive, anatase structure has not formed clearly (the base peak in range of $20 < 2\theta < 30$ is an evidence of anatase phase); but XRD measurements of other samples, with additives, have revealed that the samples 2, 3 and 4 possess an anatase structure and any evidence of rutile and mixed phases have not been observed. It has been reported that during improper heat treatment, sol-gel samples of TiO_2 undergo a phase transformation from anatase to rutile phase which in this situation have not any self-cleaning ability. Samples 2, 3 and 4 have presented different proportions of anatase phase. According to XRD patterns, anatase phase peak in sample 4 which contains HPC additive is sharper than same peak in other samples that reveals sample 4 is only in the anatase form and it is very good for self-cleaning ability.

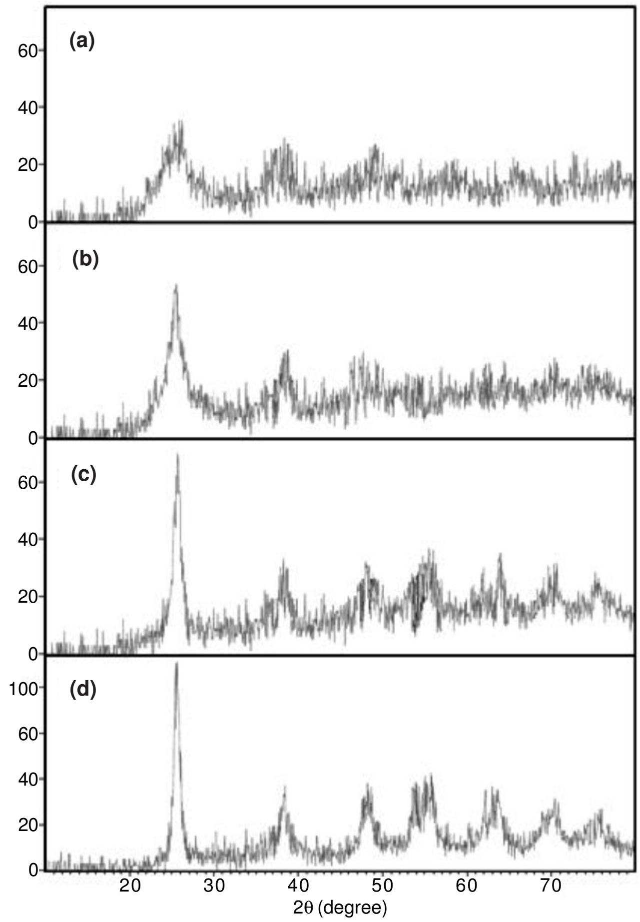

Fig. 3. XRD patterns of sol-gel synthesized TiO_2/SiO_2. (a)Sample 1, (b) sample 2, (c) sample 3, (d) sample 4

Effects of additives on the self-cleaning and photocatalitic activity: The effect of additives on photocatalytic activity has been revealed in Fig. 4. The self-cleaning ability and photocatalitic activity has increased with application of additives. According to Fig. 4, sample 4 whit HPC has the best self-cleaning activity in comparison with other samples.

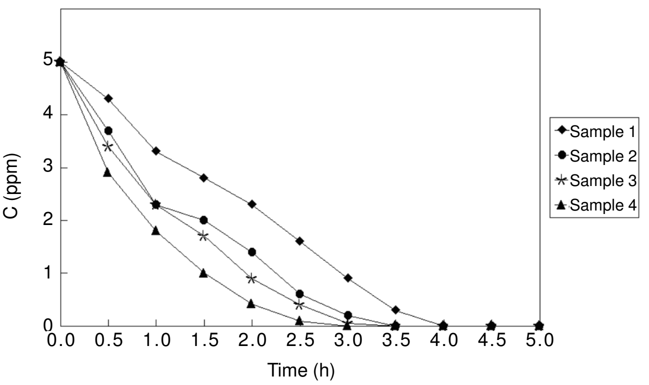

Fig. 5. Photodegradation rate of methylorange solution under UV radiation

Conclusion

Four samples of TiO_2/SiO_2 nanocomposite with self-cleaning and photocatalytic properties have been prepared by a sol-gel method. The photocatalytic properties of the synthesized nanocomposites were prepared for degradation of methyl orange in water under UV-irradiation in a batch reactor and their results showed that the photocatalytic activity of the nanocomposites have been increased, respectively by CMC, PVP and HPC. SEM pictures have revealed that the particle size of TiO_2/SiO_2 powder with HPC was smaller than other samples.

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