Materials Sciences and Applications, 2011, 2, 14-19
doi:10.4236/msa.2011.21003 Published Online January 2011 (http://www.SciRP.org/journal/msa)

Synthesis of TiO_2/Al-MCM-41 Composites with Coal-Measure Kaolin and Performance in Its Photocatalysis

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Received October 17th, 2010; revised December 13th, 2010; accepted December 21st, 2010.

ABSTRACT

TiO_2/Al-MCM-41 composites with various titania content were prepared by loading titania into the mesopores of Al-MCM-41 mesoporous molecular sieve from coal-measure kaolin as silicon and aluminum source via general sol-gel method and incipient wetness impregnation method. TiO_2/Al-MCM-41 composites were characterized by XRD, FT-IR and SEM, and the photocatalytic degradation of methyl orange solution under visible light irradiation. The results showed that the titania crystalline phase was anatase, and the particles size of TiO_2 increase with TiO_2 content. The photocatalytic degradation rates of all samples prepared by sol-gel method and incipient wetness impregnation have been become stable by visible light irradiation for 150 min, and the highest degradation rate was 83.7% and 76% respectively.

Keywords: *Coal-Measure Kaolin, Al-MCM-41, TiO_2, Photocatalytic Degradation, Methyl Orange*

1. Introduction

Kaolin, relatively pure clay, has a wide variety of applications in industry, particularly as paper mill wastewater, rubber filler, ceramic, organic matter intercalation material, adsorbent, catalyst, and cement [1-6]. Kaolin is rock comprised largely of the kaolin group mineral including kaolinite, nacrite, dickite and halloysite. The particle size of kaolin group mineral is less than 2 μm, and particle shape is flake, layer, tubular or folded sheet. The most common kaolin mineral is kaolinite ($Al_2[Si_2O_5](OH)_4$), which is a layer structure consisting of silicon oxygen tetrahedron layer and aluminum-oxide octahedral layer. Coal-measure kaolin, as one kind of kaolin, has been investigated by researchers in many fields, such as zeolites, mesoporous material, and intercalated material [7-12].

Nanoparticles of titania have a large specific surface area, which is responsible for the better performance [13,14]. Because of its wide band gap of 3.0-3.2 eV, the effective industries application of titanias gets bottle-necks. Since the discovery of mesoporous materials [15,16], MCM-41 has attracted particular attention and widely used as catalyst and hosts for nanomaterials synthesis because of their high specific surface area, uniformly pore size and uniform and ordered mesoporous channels [17-22]. In order to overcome the bottle-necks of commercials application of TiO_2 nanoparticles, there are many work focused on the loading onto MCM-41 mesoporous materials of TiO_2 nonpareils [23-25].

Long-term water shortages driven by population growth, industries pollution and climate change are forcing people to learn to live with less water and treat wastewater for circulation [26]. Wastewaters from various industries, factories, laboratories, etc. are serious problems to the environment [27]. Actually, in many cases, much industrial wastewater streams are only slightly contaminated and contain low levels of dissolved organic compounds, such as dyes. In recent years, photocatalytic degradation of dyes using MCM-41 mesororous materials loaded/doped/coated/grafted/substituted by TiO_2 nanoparticles or titanium has become very important [28-34]. However, there is no study on the photocatalytic degradation of dyes by TiO_2 loading on Al-MCM-41 mesoporous materials under visible light irradiation. It was proved that there were more solid acid sites on the surface of MCM-41 mesoporous materials if aluminum was inducted into its framework.

Our research group have devoted to the application of nature mineral, especially coal-measure kaolin. We synthesized basic molecular sieve [9], 4A zeolites [7], 5A zeolites [10] and mesoporous material [8].Here we report the formation of TiO_2/Al-MCM-41 composites using coal-measure kalin as starting materials and the photocatalytic degradation of methyl orange by these composites under visible light irradiation. We have used tetrabutyl titanate as Ti source and ethanol medium for general sol-gel method and incipient wetness impregnation method. It has been observed that the titania particles are loaded onto Al-MCM-41 mesoporous materials, which controls the particles size and narrows the band gap of titania.

2. Experimental

2.1. Raw Materials

The coal-measure kaolin was supplied from the Xuzhou COAL MINING GROUP CORPORATION (China). The chemical composite of coal-measure kaolin was determined by XRF and given as follows: SiO_2 39.24%; Al_2O_3 36.12%; CaO 0.39%; TiO_2 0.65%; K_2O 0.12%; Na_2O 1.21%; MgO 0.18%; Fe_2O_3 0.89%; ignition loss is 20.78%. Cetyltrimethylammonium Bromide (CTAB) used as template was obtained from SHANGHAI SHANPU CHEMICAL CO., LTD and NaOH was bought from Merck Company with 99.9% analytical grade. Sulfuric acid was obtained from SHANGHAI SHENXIANG CHEMICAL REAGENT CO, .LTD.

2.2. Synthesis of Al-MCM-41 Mesoporous Materials

Al-MCM-41 was synthesized through hydrothermal treatment as follows: CTAB was dissolved in deionized water. NaOH was added into CTAB solution, stirred for 30 min. The precursor prepared by selectively acid leaching method from coal-measure kaolin was then added into the mixed solution, magnetic stirring for 1 h. The mixture was then transferred into a Teflon-lined steel autoclave and kept under hydrothermal condition at 110˚C with continuous stirring (200 rpm) for 12 h. The resultant white product was filtered, washed for 3 times with deionized water, dried at 110˚C for 10 h, and calcined at 550˚C in air for 6 h to produce Al-MCM-41 mesoporous materials.

2.3. Synthesis of TiO_2/Al-MCM-41 Composites

TiO_2/Al-MCM-41 composites can be obtained with tetrabutyl titanate as Ti source. TiO_2 was introduced onto Al-MCM-41with loading of 10%, 20%, 40%, 60% and 80% by general sol-gel method. In a typical synthesis, 1.0 g Al-MCM-41 was added into ethanol and ultrasonic for 10 min. Different amount of tetrabutyl titanate was then added to ethanol and stirred for 45 min to form a solution. A certain amount of distilled water was dropped to above solution, stirred for 2 h. The white resultant product was washed and centrifuged with distilled water and ethanol for several times, dried at 80˚C for 8 h, and then calcined at 500˚C for 4h to produce TiO_2/Al-MCM-41 composites. The products are named as GS10, GS20, GS40, GS60 and GS80, where GS means as prepared by general sol-gel method, and 10, 20, 40, 60 and 80 are the Ti/Si mass ratio, respectively.

Another kind of TiO_2/Al-MCM-41 composites for comparison was prepared by an incipient wetness impregnation method. Typically the loaded process was as follows: the as-prepared Al-MCM-41 mesoporous materials were dried in a vacuum oven at 60˚C overnight, then 1.0 g dried sample was dispersed in a mixed solution containing certain amount of tetrabutyl titanate and distilled water, magnetic stirred for 2 h. The white resultant product was dried at 80˚C for 8 h, calcined at 500˚C for 4 h to produce TiO_2/Al-MCM-41 composites. The products are named as IS10, IS20, IS40, IS60 and IS80, where IS mean as prepared by an incipient wetness impregnation method, and 10, 20, 40, 60 and 80 are the Ti/Si mass ratio, respectively.

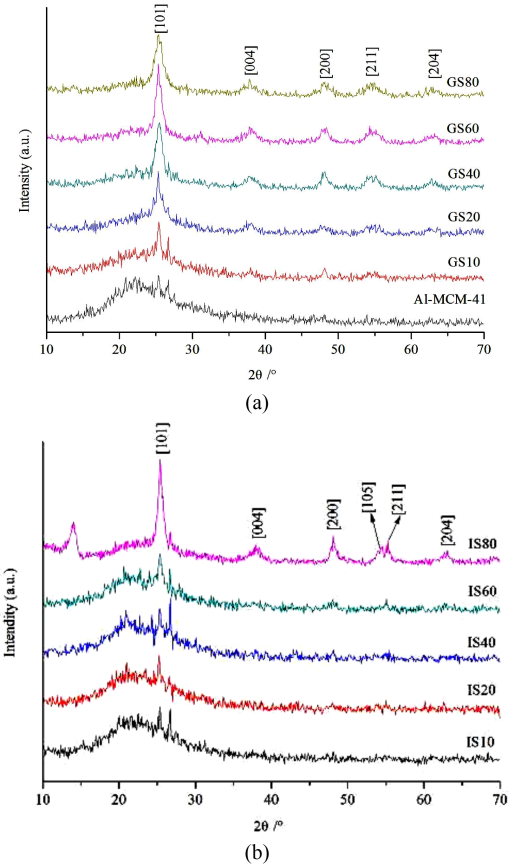
2.4. Characterization

The XRD data were collected by the Y500 full automatic diffractometer (Dandong, China) with Cu radiation at 30 kV and 20 mA (step size: 0.09˚ per step). The chemical composition of coal-measure kaolin was determined by X-ray fluorescence (ADVANT′XP, ARL, Switzerland). A Fourier transform infrared spectrophotometer, NEXUS 670 (Nicolet, USA, spectral range from 4000 cm^{-1} to 400 cm^{-1}), was used to confirm the composition of raw material, metakaolinite, precursor and the resultant material. The microstructures of the samples were observed using a QANTA200 (FEI, USA) at an accelerating voltage of 20 kV.

The photocatalytic activity of TiO_2/Al-MCM-41 composites was evaluated from an analysis of the photodegradation of methyl orange (MO) under visible light irradiation. The visible light source was a commercial 300 W halogen lamp (a cut-off filter was used to remove the light with a wavelength bellow 400 nm). 0.03 g TiO_2/Al-MCM-41 composites were ultrasonically dispersed in 20 ml methyl orange solution (50 mg L^{-1}, the pH value of MO solution was adjusted to 6 with distilled hydrochloric acid). After stirred in dark for 1 h, the adsorption/desorption of MO on TiO_2/Al-MCM-41 composites reached equilibrium. The solution was then irradiated with a visible light. The distance between MO solution and the visible light source was 20 mm. The concentration of solution was detected every 30 min with a 722N UV-visible spectrophotometer at 464 nm.

3. Results and Discussion

Figure 1(a) provides the X-ray diffraction patterns of the Al-MCM-41 mesoporous material and TiO_2/Al-MCM-41 composites prepared by general sol-gel method. The diffraction pattern for Al-MCM-41 mesoporous material has no distinctive diffraction peak at around 2θ = 10 to 70˚. On contrary, all TiO_2/Al-MCM-41 samples present distinctive peaks centered at 2θ = 26.1˚, 38.1˚, 48.1˚, 55.1˚ and 62.2˚, which correspond to the anatase (101), (004), (200), (211) and (204) crystalline planes respectively. Moreover, the intensity of all peaks of TiO_2/Al-MCM-41 composites except GS80 increases with increasing TiO_2 content, which indicates that the addition of TiO_2 content enhances the particles size of TiO_2 particles. The intensity decrease of diffraction peaks of GS80 sample may be due to the crystalline transition of a few TiO_2 from anatase to amorphous. The X-ray diffraction patterns of TiO_2/Al-MCM-41 composites prepared by an incipient wetness impregnation method are showed in **Figure 1(b)**. The diffraction patterns for IS10, IS20, IS40 and IS60 have no distinctive diffraction peak at 2θ = 26.1˚, 38.1˚, 48.1˚, 55.1˚ and 62.2˚, but the diffraction pattern for IS80 has six characteristic diffraction peaks of anatase TiO_2. This can be complained that TiO_2 particles enter into the pore channel of Al-MCM-41 mesoporous material when the content of TiO_2 is low, but TiO_2 particles are loading onto the surface of Al-MCM-41 mesoporous material when the content of TiO_2 increase to 80%.



(a)

(b)

Figure 1. XRD patterns of Al-MCM-41 mesoporous material and TiO_2/Al-MCM-41 composites prepared by (a) General sol-gel method and (b) An incipient wetness impregnation method.

The FT-IR spectra of Al-MCM-41 mesoporous material and TiO_2/Al-MCM-41 composites prepared by general sol-gel method are showed in **Figure 2**. The vibration band at 456, 797, 958 and 1230 cm^{-1} in Al-MCM-41 mesoporous material assign to bending vibrations of Si-O, vibrations of Al-O-Si, vibrations of Si-OH, vibrations of Si-O-H, respectively. The bands at 3450 and 1638 cm^{-1} are assigned as stretching vibrations of -OH. The strong vibration band, which at 1078 cm^{-1} in Al-MCM-41 sample assign to asymmetric stretching of Si-O-Si, has shifted to 1094 cm^{-1} in TiO_2/Al-MCM-41 samples. Wave number for asymmetric stretching of Si-O-Si has shifted from lower to higher value when titanium was loaded onto Al-MCM-41. The strength of vibration band at 797 and 1230 cm^{-1} in Al-MCM-41 sample, which assigned to stretching of Al-O-Si and Si-O-H respectively, have decreased with increased titanium load. In our samples, peak around 910 ~ 960 cm^{-1} which due to the Si-O stretching vibration of a polarized Si-O-Ti bond [10-12,22] has not been observed. But it is observed that peak at 958 cm^{-1} in Al-MCM-41 sample assign to free vibration of Si-OH is narrow and more intense as compared to the TiO_2/Al-MCM-41 composites samples. This may duo to the weak bond of Si-O-Ti [14].

Figure 3 shows SEM micrographs of the prepared samples. The layered Al-MCM-41 mesoporous material

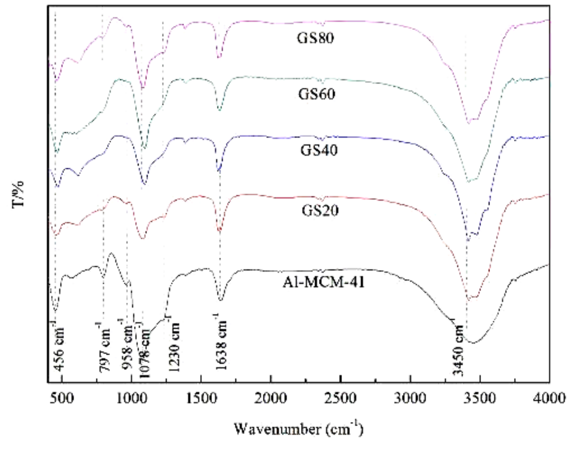
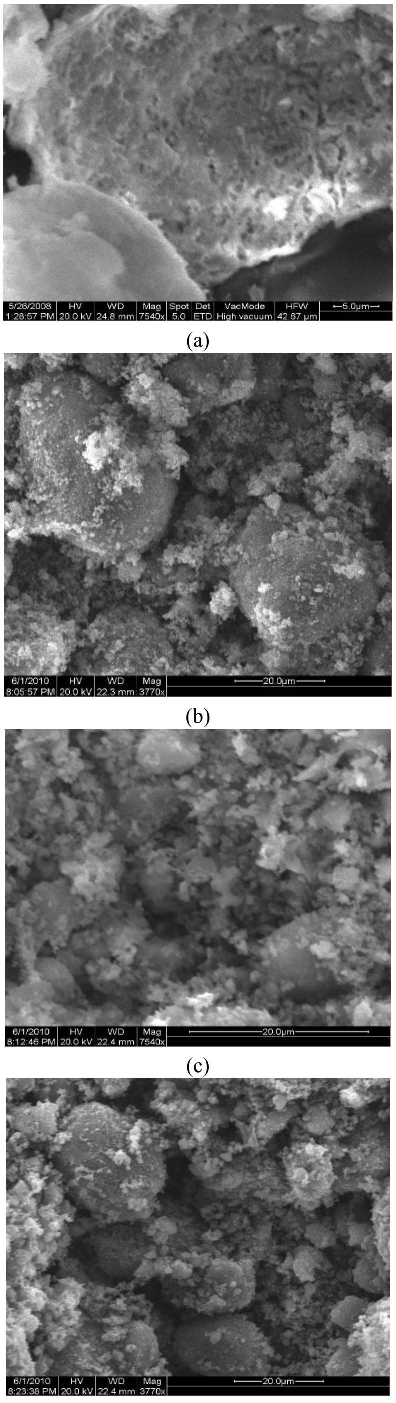


Figure 2. FT-IR spectra of Al-MCM-41 and mesoporous material and TiO_2/Al-MCM-41 composites.



(a)

(b)

(c)

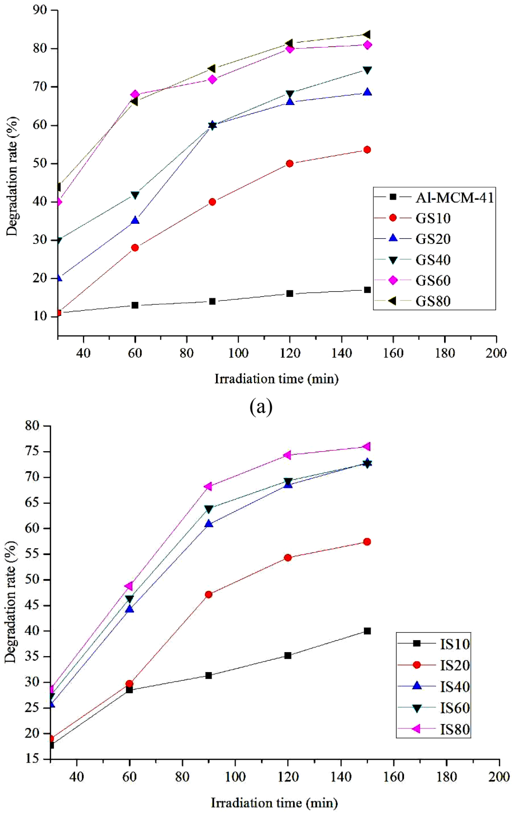
(d)

Figure 3. SEM micrographs of prepared samples. (a) Al-MCM-41; (b) IS40; (c) IS80; (d) GS80.

takes on an overlapped worm-like structure can be obviously confirmed by SEM, as shown in **Figure 3(a)**. **Figure 3(b)** shows SEM image of rod-like particles of IS40 sample, the shape change from layer to rod-like may be due to titanium coating on mesoporous material. **Figure 3(c)** shows SEM image of IS80 sample and **Figure 3(d)** shows SEM image of GS80 particles. The titanium powders are found to be fine and slightly agglomerated.

The photocatalytic degrading curves of methyl orange are displayed in **Figure 4.** It is found that after the prepared samples have been dispersed into the methyl orange aqueous solution for few time under no light irradiation, which is not shown here, a decrease in the concentration of methyl orange solution occurred, which is attributed to the adsorption of the prepared samples for methyl orange molecules. It can be seen that the photocatalytic degrading rates increase with visible light irradiation time, and the degrading rates of GS sample are higher than IS particles. For example, after irradiation for 150 min, the photocatalytic decomposition rate of GS10, GS20, GS40, GS60 and GS80 are 53.6%, 68.5%, 74.6%, 81% and 83.7%, respectively; at the same time, the degrading rate of IS10, IS20, IS40, IS60 and IS80 are only 40%, 57.4%, 72.8%, 73.7% and 76%, respectively. This may due to the uniformity loading of TiO_2 particles by general sol-gel method on Al-MCM-41 mesoporous material and slightly agglomerated.

The photocatalytic degrading rates are lower than the results of some reports [30,31,33], which the catalyst was irradiated under ultraviolet light, loaded by mesoporous



(a)

(b)

Figure 4. Photocatalytic degrading curves of methyl orange. (a) GS samples; (b) IS samples.

TiO_2 or modified TiO_2 with other ions doped respectively.

4. Conclusions

TiO_2/Al-MCM-41 composites with different ratios of TiO_2 using coal-measure kaolin as starting materials were prepared at room temperature in ethanol solution by general sol-gel method and incipient wetness impregnation method. The photocatalysis properties of these composites were also studied by photocatalytic degradation of methyl orange visible light irradiation. The results showed demonstrate that TiO_2 nanoparticles enter into the pore channel of Al-MCM-41 mesoporous material and enhance the photocatalysis property of this material. TiO_2/Al-MCM-41 composites can degrade methyl orange under visible light irradiation. The degradation rate of methyl orange under visible light irradiation of TiO_2/Al-MCM-41 composites prepared by general sol-gel method is higher than the rates of IS sample at the same time.

5. Acknowledgements

This work was supported by the Research fund for Social Development Plan of the Science and Technology Department of Jiangsu provincial government (BS2007 038).

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