Preparation, Characterization of Supported Phosphotungstic Acid and Photocatalytic Degradation of Aqueous Methyl Orange

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In this paper, phosphotungstic acid was immobilized into mesopore materials MCM-41 with a larger surface area and a higher thermal stability. The supported phosphotungstic acid catalysts were characterized by FT-IR, TEM and N_2 adsorption-desorption techniques. In addition, the effect of supported contents of the phosphotungstic acids on the degradation rate was also studied.

Keywords: Methyl orange, Phosphotungstic acid, Photo-catalysis.

INTRODUCTION

Due to the specific structure and properties of heteropoly compounds, people have focused on its catalytic research in recent years[1-3]. Different species of cation and metal have been designed[4-5] and varieties of catalysts for specific functions have been synthesized[6-7]. Since heteropoly compounds have a unique structure, oxidiability and photochromism, they are starting to be used in the photocatalytic degradation of pollutants. In this paper, a supported phosphotungstic acid (HPW) catalyst was prepared by the impregnation method and characterized by FT-IR, TEM, XRD and BET-BJH. A 250 W mercury lamp was used as the light source and methyl orange solution was used as degradation sample. The effect of different amount of loaded phosphotungstic acid on the catalyzation of the degradation of methyl orange solution was studied. The effects of the different reaction conditions which influenced the efficiency of the degradation of methyl orange solution were also investigated.

EXPERIMENTAL

Preparation of MCM-41: 4.8 g of CTAB and 0.44 g of NaOH were added to 24 mL of distilled water. The mixture was stirred at 40 °C. Afterwards, 5 mL of TEOS was slowly added and vigorously stirred for 3 h. Then the mixture was transferred into a Teflon-lined, stainless steel autoclave where it wa aged at 110 °C for 24 h. After cooling down to room temperature, the solid was filtered, washed with a large amount of deionized water and dried at room temperature. As-synthe-sized sample was calcined at 550 °C for 6 h to obtain the resulting sample of MCM-41.

Different amounts of loaded phosphotungstic acid catalyst preparation: To prepare different concentrations of phosphotungstic acid (HPW), 0.11, 0.43, 1 and 2.33 g of phospho-tungstic acid were dissolved into 25 mL of distilled water, respectively. 1 g of MCM-41 was added to each concentration of phosphotungstic acid. The mixture was stirred at 80 °C until the distilled water dried up. The samples obtained were denoted as 10 % HPW-MCM-41, 30 % HPW-MCM-41, 50 % HPW-MCM-41 and 70 % HPW-MCM-41, respectively.

Characterization of the samples: Fourier transform infrared (FT-IR) spectra of the skeletal vibration of the materials were recorded using a KBr flake on a Shimadzu Nicolet Avatar 370 DTGS spectrometer. N_2 adsorption/desorption isotherms were recorded at 77 K with a Micromeritics ASAP 2010. Before measurements, samples were outgassed at 573 K for 3 h. BET surface areas (S_{BET}) were calculated from adsorption branches in the relative pressure range of 0.05 to 0.30. Pore size distributions were calculated from adsorption branches using the Barret-Joyner-Halenda (BJH) method. The mesopore surface area and pore volume were calculated by the t-plot method. Transmission electron micrographs (TEM) were analyzed with a Hitachi H-8100 electron microscope operated at an accelerating voltage of 100 kV.

RESULTS AND DISCUSSION

N_2 adsorption-desorption studies: Fig. 1 (A) displays the N_2 adsorption-stripping isotherm of the carrier of MCM-41 and different amounts of loaded HPW catalyst in liquid nitrogen temperature. From the isothermal curve, it can be observed that when the specific pressure (P/P_0) is between

0.5 and 0.9, there is a closed hysteretic loop between the isothermal curve of the carrier and HPW-loaded-catalyst. According to the division of BDDT standard, the curve can be attributed to type IV, which is a typical mesoporous material and indicates that the mesoporous structure still exist in the HPW-loaded-catalyst. With the increase of the amount of HPW, the amount of N_2 adsorption decrease and the hysteretic loop can be attributed to type H_2. With the increase of relative pressure, all of the curves have a rapid capillary condensation which shows that all the samples have a uniform distribution of the mesoporous channel, not destroyed by the loaded HPW.
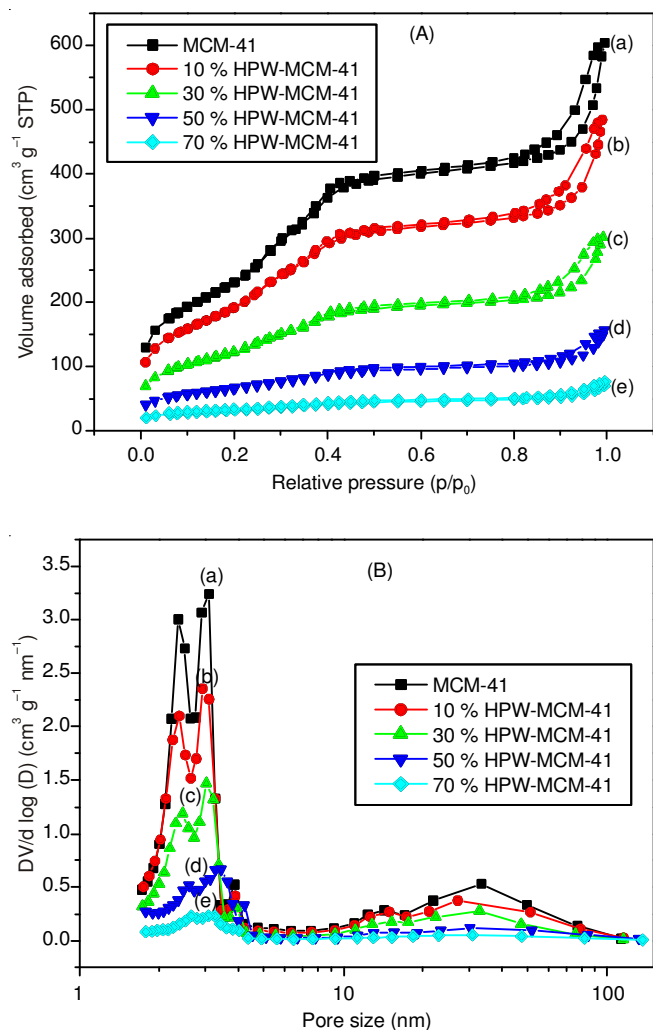

Fig. 1. N_2 adsorption-desorption isotherms (A) and the pore size distribution (B) of the carrier of MCM-41 and different amount of loaded HPW catalyst

Fig. 1 (B) displays the pore size distribution of MCM-41 and the different amounts of the loaded HPW catalyst. When the amount of loaded HPW increased, the pore size of the carrier decreased gradually, which indicates that the HPW was loaded on the inner surface of the carrier successfully. In the diagram, the pore size of the carrier can also be measured clearly when the amount of loaded HPW was up to 50 %. However, it is difficult to measure the pore size of the carrier when the amount of loaded HPW was up to 70 %, which indicates that the particles of the phosphotungstic acid blocked the channel of MCM-41.

FT-IR studies: The FT-IR diagram of MCM-41 and the different amounts of loaded catalyst is shown in Fig. 2. The absorption peak of the carrier at 1080 cm^{-1} can be attributed to the Si-O-Si antisymmetric stretching vibration of the skeleton of the molecular sieve. The 800 and 450 cm^{-1} infrared absorption peaks were attributed to the Si-O-Si symmetric stretching vibration and bending vibration, respectively. The absorption peak at 3450 cm^{-1} indicated that the hydroxyl group exists on the surface of the molecular sieve channel[8]. Due to the large amount of the hydroxyl group, intermolecular hydrogen bond was present, which made the intensity of the absorption peak bigger and wider. When the capacity was up to 10 %, the 800 and 450 cm^{-1} absorption peak did not appear, which can be attributed to the structure of Keggin asymmetry vibration absorption. When the capacity was up to 30 %, the specific infrared absorption peak of HPW at 989 and 898 cm^{-1} were observed clearly. With the capacity increase, the intensity of the absorption peak also increased. Moreover, the intensity of P-Oa and W-Oc-W characteristic absorption peak of 30% HPW-MCM-41, 50 % HPW-MCM-41 and 70 % HPW-MCM-41 were bigger than pure phosphotungstic acid. It can be explained that the carrier of Si-O-Si has a strong vibration peak at 1080 and 800 cm^{-1}, which overlays the absorption peak of P-Oa and W-Oc-W separately.
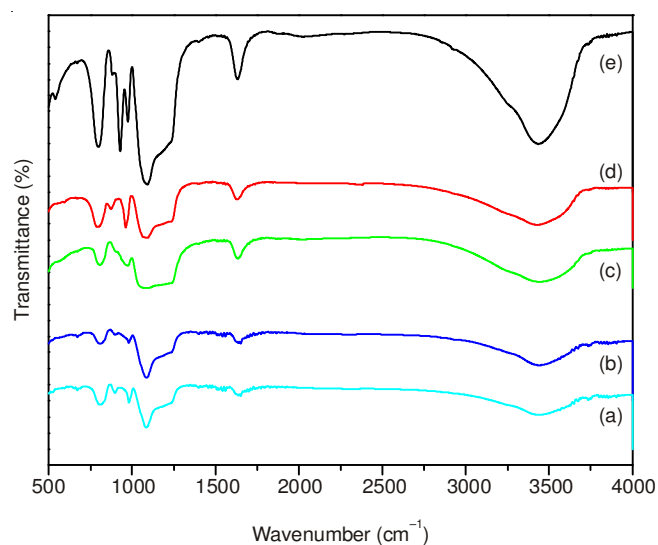

Fig. 2. FT-IR spectra of the samples: (a) MCM-41, (b) 10 % HPW-MCM-41, (c) 30 % HPW-MCM-41, (d) 50 % HPW-MCM-41, (e) 70 % HPW-MCM-41

Catalytic degradation of methyl orange: Fig. 3 showed that when the concentration of methyl orange at 0.008 g/L had an insignificant effect on the catalyst (10 % HPW-MCM-41). The degradation rate was only 15 % after 140 min of illumination.

The degradation rate of methyl orange solution (catalyst 30 % HPW-MCM-41, 50 % HPW-MCM-41, 70 % HPW-MCM-41) also increased with the increase of illumination time. Catalyst 70 % HPW-MCM-41 was the best for degrading the methyl orange solution. After 120 min of illumination, the degradation rate of the methyl orange solution reached 92 %.
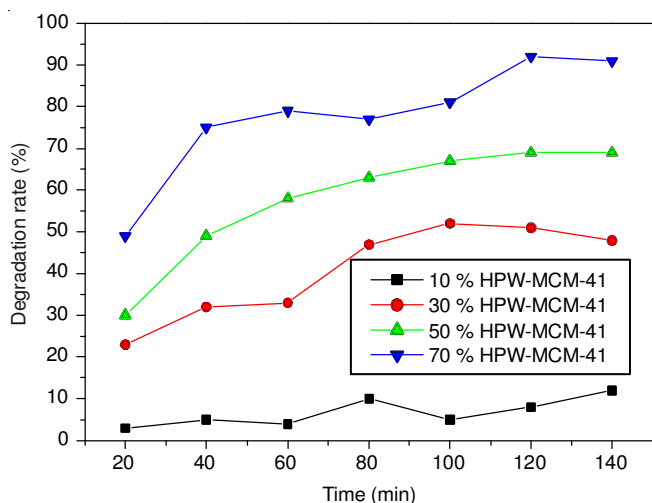
Conclusion

The MCM-41 carrier was synthesized through the hydro-thermal method. The different capacities of phosphotungstic acid were synthesized through the dipping method. The BET-BJH, FT-IR and TEM method were used to characterize the different synthetic samples. The results show that the HPW had been loaded on the surface of the MCM-41 successfully and had a great effect on the photocatalytic degradation of the methyl orange solution.

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