Photocatalytic effects of heteropolytungstic acid - encapsulated TiSBA-15 on decomposition of phenol in water

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TiO_2 has been used as photocatalyst since two and half decades ago. The efficiency in its photocatalytic reactions has been improved by increasing the surface area of the photocatalyst by supporting fine TiO_2 particles on some porous materials. In this work, heteropolytungstic acid (HPA) - encapsulated into the titanium exchanged SBA-15 mesoporous materials (TiSBA-15) were prepared and characterized. Also their photocatalytic effects on decomposition of phenol were investigated and the photodecomposition rates of the phenol were observed to be increased by 2.5 8 fold, as compared to those observed in the presence of HPA-encapsulated SBA-15 or TiSBA-15 without HPA.

key words: TiSBA-15, Heteropolyacid, Photocatalytic reaction, Phenol

INTRODUCTION

Silica based, mesoporous materials have generated a great deal of interest in their application in the field of catalysis, sensing, guest-host chemical supporters and adsorption due to their high surface areas and large ordered pores ranging from 20 to 300 Å [1-7]. Compared to the crystalline microporous materials, the mesoporous materials have some disadvantages [8]. In order to overcome the disadvantages, efforts have been made by many researchers to introduce metal ions (Ti, Al, or V) into the mesoporous materials to effectively increase the catalytic activities [9-11]. Among the metal ions supported microporous and mesoporous materials, titanium substituted microporous and mesoporous materials were found to be effective catalyst for selective oxidation of a variety of organic compounds in dilute hydrogen peroxide [12], photocatalyst [13,14] and catalytic support [15]. This is because TiO_2/SiO_2 supported oxides have been considered as advanced support materials as substitutes for pure TiO_2, which improves the mechanical strength, thermal stability and surface area of the metal oxides (TiO_2). The high activity of such materials has been attributed to more accessible titanium sites or to a decrease in the silanol concentration [16,17].

Heteropoly acids (HPA) also offer a wide range of characteristics such as molecular composition, size, shape, charge density, redox potentials, acidity and solubility that render them potentially promising catalysts. In addition, the heteropoly acids can accept and release a certain number of electrons without decomposition [18-20]. It is well known that ligand to metal charge transfer takes place on illumination (< 400 nm) of heteropoly acids and also generates strongly oxidizing excited state [21]. Many authors demonstrated the ability of heteropoly acids as catalysts in the preparation and decomposition of many organic compounds [22-25]. Also by supporting HPA on the solid surface, their specific surface area is known to be largely increased [23]. This greater surface area may result in an increase in the catalytic activity of HPA by providing more contact area between catalyst and substrate for the surface mediated electron transfer reactions to take place. Based on the above concept, Zheng *et al.* [26] observed enhanced catalytic activity in the conversion of organic molecules when photosensitive molecules like Heteropolyacid $(PW_{12}O_{40})^{3-}$ (HPA) were loaded into SBA-15.

In this work, we have studied the preparation and characterization of the HPA-encapsulated into SBA-15 and TiSBA-15 frameworks with the aim to observe the photo-induced interfacial electron transfer from the titanium in TiSBA-15 to the encapsulated HPA, which induces the synergistic enhancement of the catalytic activity in the photooxidation of phenol dissolved in water.

MATERIALS AND METHODS

Materials

The chemicals used are titanium isopropoxide, sodium tungstate, phenol were purchased from Aldrich. All the other chemicals used were purest research grade available. XRD diffraction data were collected by using MO3X-HF diffractometer (Model-1031, Mac Science Co.). Nitrogen adsortion isotherms

were measured at 77 K using a Micromeritics apparatus.

Diffused reflectance UV-Vis spectra of the samples were recorded using a Shimadzu UV-3101PC spectrophotometer equipped with an integrating sphere. IR spectra are recorded with a JASCO FT/IR 410 spectrophotometer by employing KBr pellet technique. 161.921 MHz ^{31}P NMR MAS spectra were recorded at room temperature on a Bruker (DSX 400) spectrometer using H_3PO_4 as external reference.

For the photooxidation processes of phenol, the sample was illuminated with both UV light (Rayonet Photochemical reactor, USA, 8.124×10^{-8} einsteins/cm^2/s) and visible light (150 W Xenon arc lamp, 2.443×10^{-9} einsteins/cm^2/s) in the presence of 100 mg of the catalysts. The apparent kinetics of disappearance of the substrate phenol was determined by following the concentration of the substance at various time intervals using high performance liquid chromatography (HPLC). The HPLC assembly consisted of a Waters 2690 HPLC pump, X Terra™ C-18 column and Waters 996 PDA detector. The detection wavelength was 260 nm. The mobile phase consisted of a 40:60 methanol-water mixture.

Preparation of the photocatalyst

Mesoporous SBA-15 was prepared by using microwave as reported previously [7, 27]. In order to prepare TiSBA-15, 6 wt % titanium was added in the synthetic processes of SBA-15, followed by hydrothermal treatment for 24 hrs [28, 29]. Encapsulation of HPA in the SBA-15 or TiSBA-15 frameworks was carried out by an *in situ* synthesis of this compound in a similar manner to Bailar *et al.* [30] procedure for the synthesis of HPA (i.e., the ratio of sodium tungstate and disodium phosphate 1:1/12). The preparation procedure is as follows: 2 g of SBA-15 or TiSBA-15 was added to a solution of disodium phosphate [$Na_2HPO_4.12H_2O$; 0.5195 g] in water and the whole mixture was stirred to 2 hrs at ambient temperature. Then a solution of sodium tungstate (Na_2WO_4. $2H_2O$; 14.693 g) was added drop wise to the suspension. After 1.5 hrs of stirring, a stoichiometric amount of HCl was added drop wise. The suspension was stirred further for 4 hrs. Finally, the mesoporous materials was separated from liquid and washed very intensively with hot doubly distilled water.

RESULTS AND DISCUSSION

Characterization of the photocatalyst

The structure and quality of the prepared SBA-15 or TiSBA -15 were confirmed by both XRD and N_2-adsorption isotherms, consistent with those reported previously [27-29]. Figure 1 shows the XRD patterns of SBA-15 and TiSBA-15, demonstrating that frame of SBA-15 is not changed upon addition of TiO_2. Figure 2 shows the nitrogen adsorption isotherms for SBA-15 or TiSBA-15. These data were analyzed to determine a d_{001} of 10.6 nm with pore size of 9.5 nm as determined by Breck model [2].

The infrared spectroscopy is a useful technique for characterizing the mesoporous materials like SBA-15 or TiSBA-15 materials
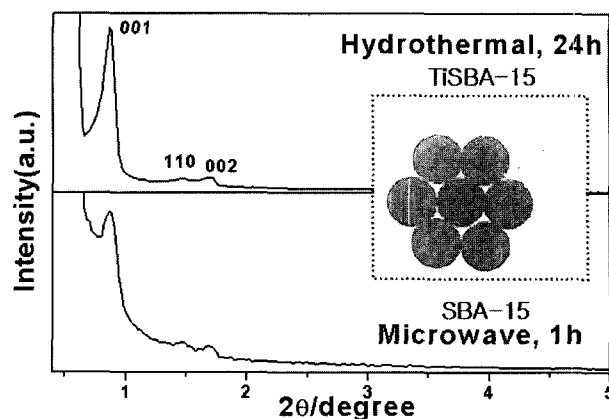

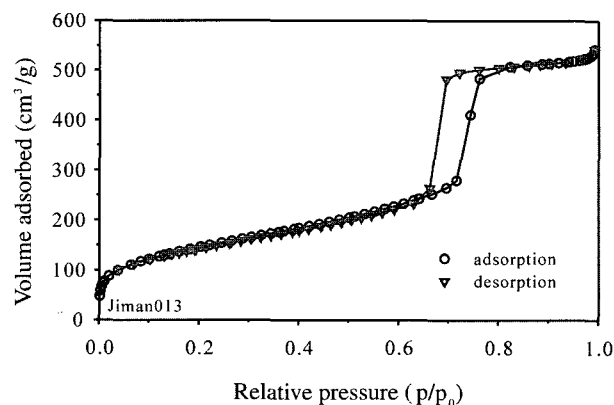Figure 1. XRD patterns of SBA-15 and TiSBA-15

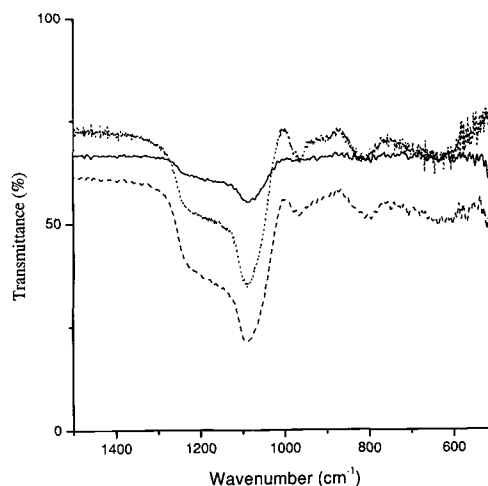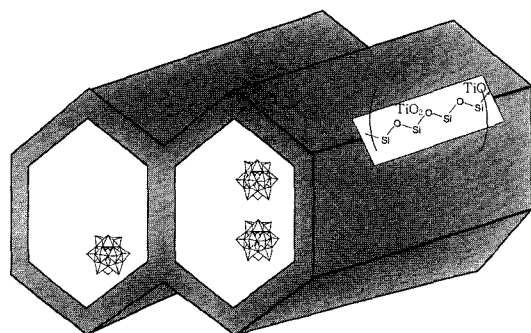Figure 2. Nitrogen -adsorption isotherms on SBA-15 or TiSBA-15

Figure 3. IR spectra of SBA-15 without HPA (——), HPA-encapsulated SBA-15 (- - - -) and HPA encapsulated TiSBA-15 (···).

and their spectra's were already explained in detail by many authors [29, 31-33]. As shown in Figure 3, pure silica exhibits the symmetrical Si-O-Si stretching vibration at 815 cm^{-1}, along with a very weak band at 980 cm^{-1} due to the symmetric stretch of Si-OH groups. The addition of titanium surface

oxide species decreases the 980 cm^{-1} band, and a new broad band appears at 965 cm^{-1}, which is associated with the formation of Ti-O-Si bridges [34-36]. Infrared analysis of the encapsulated heteropolyacids in the mesoporous cavities confirmed the presence of the finger print bands below 1100 cm^{-1}, which are characteristic of the $PW_{12}O_{40}{}^{3-}$ ion i.e., the Keggin unit. IR spectra recorded for the encapsulated HPA into SBA-15 or TiSBA-15 shows absorption bands at 1088, 965 and 810 cm^{-1}, which are typical of Keggin unit as well as the titanium exchanged SBA-15 (Figure 3). The peak at 1088 cm^{-1} are assigned to M-O stretching (where M=P/Ti) and the peak at 965 cm^{-1} may be M=O stretching (where M=W). The other peak (810 cm^{-1}) may be due to M-O-M vibrations (where M=Si, Al, W). The fact that all the peaks are found to be overlapped over the other leads to conclude that both the exchanged titanium and the encapsulated Keggin units are present in the SBA-15 cavity similar to zeolite cavity [37-40] (See scheme 1).

In order to further confirm the prepared novel photo-catalyst, we measured NMR for all the prepared samples. The ^{31}P-NMR MAS spectra of the sample are shown in Figure 4. Pure crystals of the heteropolytungstate gave a sharp single peak at -14.799 ppm [41] whereas the encapsulated HPA into SBA-15 or TiSBA-15 shows multiple peaks from 3.3 to -14.1 ppm. The observed multiple peaks for the HPA encapsulated SBA-15 or TiSBA-15 suggest that the Keggin unit is present in the mesoporous cavity. Such broad peaks may be due to the distortion of isotropic chemical shifts of ^{31}P due to various electronic environments of HPA adsorbed in the mesoporous cavities and also due to the various number of water molecules in the proximity of the polyanion [37, 38, 42-44].

Figure 5 shows the diffused reflectance spectra of HPA-encapsulated TiSBA-15, which is different from that of the HPA - encapsulated SBA-15 and SBA-15 or TiSBA-15 without HPA [29,31]. It is interesting to notice that the absorption maximum of TiO$_2$ in SBA-15 is observed at 230 nm which is much shorter than that of anatase TiO$_2$ crystal. This suggests that nano-sized TiO$_2$ is adsorbed on inside channel of SBA-15, showing quantum effects. Also the absorption spectrum of TiSBA is red shifted (400 nm) and broadened upon addition
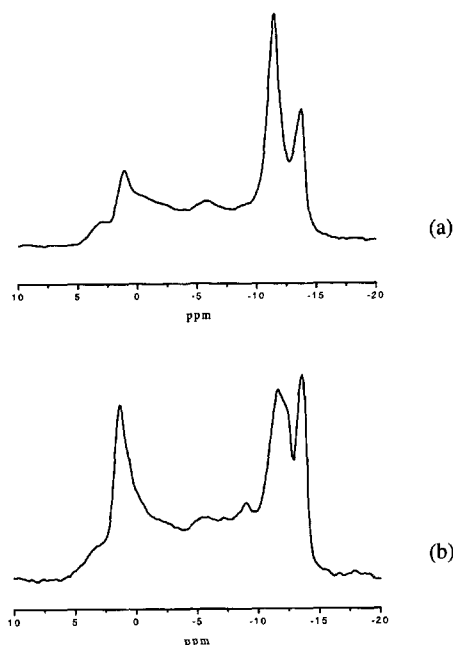

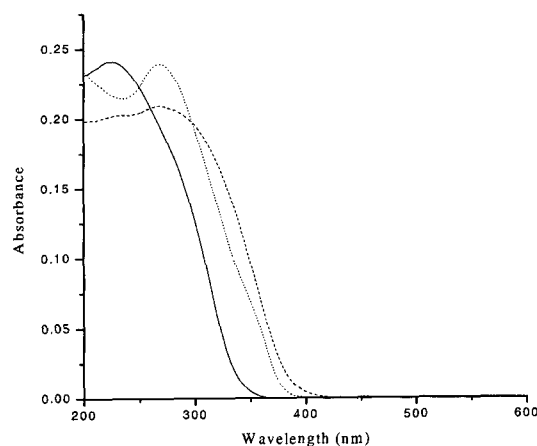Figure 4. ^{31}P MAS NMR spectra of: (a) HPA-encapsulated into SBA-15 (b) HPA-encapsulated into TiSBA-15

Figure 5. UV-Vis diffused reflectance spectra of: TiSBA-15 without HPA (——), HPA-encapsulated SBA-15 (-----) and HPA-encapsulated TiSBA-15 (·······)

of HPA, indicating that HPA is adsorbed on TiO$_2$ in SBA-15.

Photooxidation of phenol

Photolysis of phenol (1 × 10^{-3} M, 30 ml) in oxygenated aqueous solutions at pH=1 (pH adjusted with HClO$_4$) was performed in the presence of HPA-encapsulated SBA-15 or TiSBA-15 catalyst (100 mg). Figure 6 shows the photocatalyzed disappearance of phenol at various time intervals by high performance liquid chromatography. Hydroquinone and benzo-quinone were the detectable products, but they occurred only in low yields. The linear plots in Figure 6 indicate that the reaction follows first order kinetic behaviour. Similar experiments were performed for the SBA-15 or TiSBA-15 without HPA,
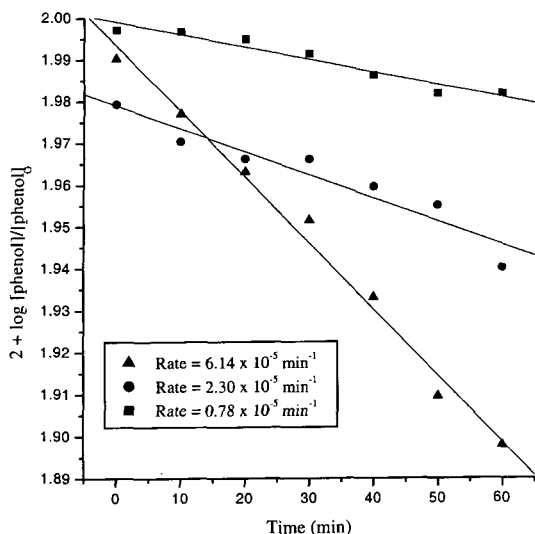

Scheme 1. Layout of the HPA-Encapsulations Ti SBA-15.

Figure 6. Comparison of photooxidation rate of phenol in the presence of: HPA- encapsulted TiSBA-15 (▲) , HPA-encapsulated SBA-15 (●) and TiSBA-15 without HPA (■). Concentrations of both catalyst and [phenol] is the same (100 mg, 1×10^{-3} M).

Scheme 2. Proposed photocatalytic cycle of HPA-encapsulated TiSBA-15

but no photocatalytic reaction was observed in the case of SBA-15 without HPA. The reaction rate was calculated for all the systems and it follows the order HPA-encapsulated TiSBA-15 > HPA-encapsulated SBA-15 > TiSBA-15 respectively. Among the systems, the HPA-encapsulated TiSBA-15 photo-oxidized phenol eight fold more effectively compared to the TiSBA-15 without HPA and 2.5 times as high as that on the HPA-encapsulated into SBA-15. Typically, photocatalytic activity for the supported photocatalysts increases with catalyst loading.

Catalytic properties of HPA-encapsulated TiSBA-15 is almost similar to the HPA without mesoporous particles described by Papaconstantinou et al. [45] in the mineralization process of phenol. According to Ferry et al., [25] the photocatalytic oxidation of organic substrate by heteropoly acid supported on the NaY zeolite is a cyclic process, typified by the application of a photoactive material to facilitate the transfer of electrons from an organic substrate to an inorganic electron acceptor as dioxygen. Similar to the semiconductor photocatalysts, they proposed photocatalytic cycle of HPA i.e., illumination of the ligand-to-metal charge transfer band of HPAs generates a strongly oxidizing excited state HPA^*. After oxidizing the electron donor, the corresponding HPA_{red} returned to the original state by an electron acceptor such as dioxygen. There can also be possibility of adsorption of substrate and photocatalyst, which also generates HPA_{red} on illumination. In addition to the above facts, the photoinduced interfacial electron transfer takes place from the TiO_2 in SBA-15 to the encapsulated HPA as observed in HPA-adsorbed TiO_2 colloids [46], which enhances the mineralization of phenol. All three possibilities lead us to propose the catalytic mechanism of HPA-encapsulated Ti-SBA-15 as shown in scheme 2.
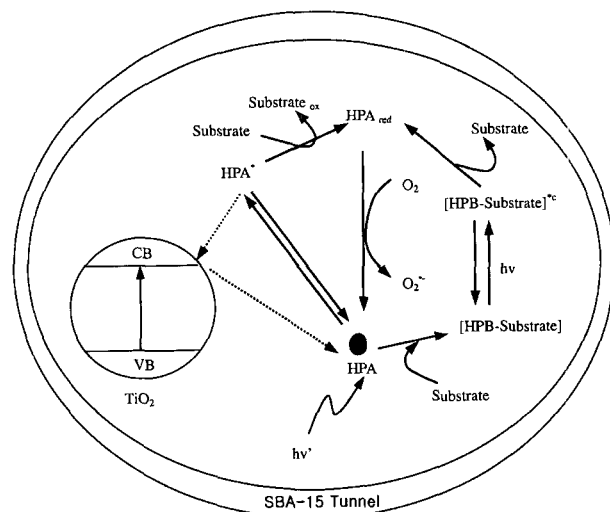
CONCLUSION

The HPA-encapsulated into TiSBA-15 is very active as a photocatalyst towards the photooxidation of phenol. Undoubtedly, the mesoporous matrix provides a better dispersion of active titanium sites thereby facilitating the photocatalytic activity. The present work, however, may serve as a preliminary step towards designing further studies on the photophysical and photochemical aspect, being under scrutiny in our laboratory at present.

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