Materials Research, Vol. 12, No. 4, 411-414, 2009

Synthesis and Characterization of a Novel Mesoporous Mn – Organophosphate Molecular Sieve

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Received: March 20, 2009; Revised: August 5, 2009

A novel mesoporous Mn – organophosphate was synthesized for the first time. It is characterized by several physicochemical techniques. Small angle X-ray diffraction analysis shows the first peak in 2.5^o with 39 A^o pore width. Elemental analysis shows that the composition is $[(C_{12}H_{23}N)_3PO]^{40}Mn$. Scanning electron microscopic picture shows the flag morphology with 1-15 µm particle size. Thermogravimetry/Differentaial thermal analysis shows almost 80% exothermic weight loss. Nitrogen adsorption isotherm shows type III with 300 m^2/g BET surface area. Fourier transform Infrared spectroscopic analysis shows that the framework vibrations are comparable to other well known silica mesoporous materials. Electron spin resonance spectroscopic analysis shows the absence of hyperfine splitting indicates the presence of Mn^{3+} species. Ultraviolet – visible spectroscopic analysis shows that most of the Mn is in tetrahedral co-ordination beside small square pyramidal species. A plausible synthesis mechanism also proposed.

Keywords: *mesoporous, Mn - organophosphate, characterization*

1. Introduction

Mesoporous materials are popular due to their high surface area and unique morphology[1-10]. The known variety of mesoporous materials are few, namely MCM-41, MCM-48 and SBA-15. The main draw back in these materials synthesis is their prolonged crystallization, low yield and high cost of reagents. There are several efforts were made in this direction to solve these problems. Recently, organophosphates were synthesized and reported[11-13] to have properties similar to zeolites. Compared to zeolites, they are prepared in short time, low cost and high yield. However mesoporous organophosphate molecular sieves are not reported so far. Beside pure organophosphate molecular sieves are not suitable for redox type catalyzed reactions. To prepare redox catalyst, a metal oxide has to be either supported or incorporated inside the structure. As the supported metal oxides is leachable to liquid phase oxidation reactions. It is necessary to prepare metal incorporated molecular sieves. There are several metal incorporated[14-38] molecular sieves are reported in literature. But there is less studies on Mn containing molecular sieves[12]. In the present study, we have synthesized Mn – containing mesoporous organophosphate for the first time and it is characterized in detail.

2. Experimental

In a typical procedure to synthesis mesoporous Mn-organophosphate, the manganese acetate (P/Mn = 40, Aldrich, USA) was dissolved in othophosphoric acid (85%, s.d.fine, India). To this mixture, 1:4 molar ratio of Dodecylamine (98%, Aldrich, U.S.A) was added and stirred well. A pink solid was resulted. The ground solid was dried at 80 °C for 12 h. The resulting solid was subjected to following physicochemical characterizations.

The above samples were analyzed for qualitative phase identification by small angle X-ray powder diffraction (Rigaku, Model D/MAX III VC, Japan, Ni filtered Cu-Kα radiation, $\lambda = 1.5404$ Å). The morphology of the organophosphate was investigated using a scanning electron microscope (JEOL®, JSM 5200). Transmission electron micrographs (TEM) of the samples were scanned on a JEOL JSM-2000EX electron microscope operated at 200 kV. Simultaneous Thermogravimetry/Differential thermal analysis of the crystalline phases was performed on an automatic derivatograph (Setaram TG-DTA 92). The adsorption and desorption measurements were carried out using an Autosorb – 1 instrument. The Fourier transform infrared spectroscopy was recorded in the diffuse reflectance mode using a 300:1 ratio sample in KBr (Nicolet 60SXB). Electron spin resonance spectra of the as-synthesized Mn - organophosphate was obtained using Bruker ER 200D spectrometer. The spectra were recorded at room temperature as well as at liquid nitrogen temperature. The spectra were recorded (with a mid range of 4000 G) in the scan range of 0 to 8000 gauss and magnetic field strength was 9.74 GHz. The Ultraviolet - visible diffuse reflectance spectra were recorded using a Pye Unichem (SP-8-100) spectrometer in the 200-800 nm regions.

3. Results and Discussion

The X-ray diffraction pattern of the Mn – organophosphate (Figure 1) shows the peaks at 2.6 (54%), 3.8 (46%), 5.3 (29%), 7.7 (100%) and 8.0 (71%). The appearance of peaks at low angle region in equal distance shows that the Mn-organophosphate is mesoporous lamellar type. The X-ray diffraction pattern is stable up to 200 °C. From the interplanar distance (d) analysis, the pore openings are calculated as 3.9 nm (39 $A^{o.}$)[39]. Elemental analysis shows that the Mn - organophosphate has composition, $[(CH_3\text{-}(CH_2)_{11}NH)_3PO]^{40}$ Mn.

Scanning electron micrograph of mesoporous Mn - organophosphate (Figure 2a) shows that the particle size is not uniform (1-15 µm),

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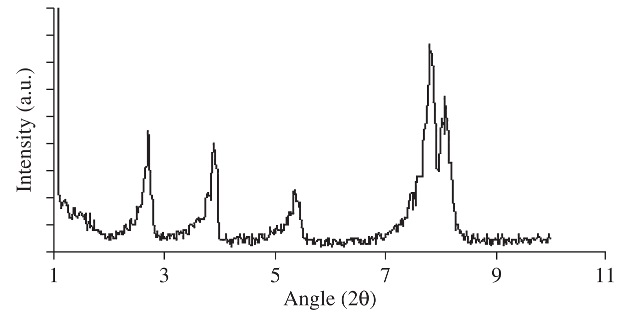
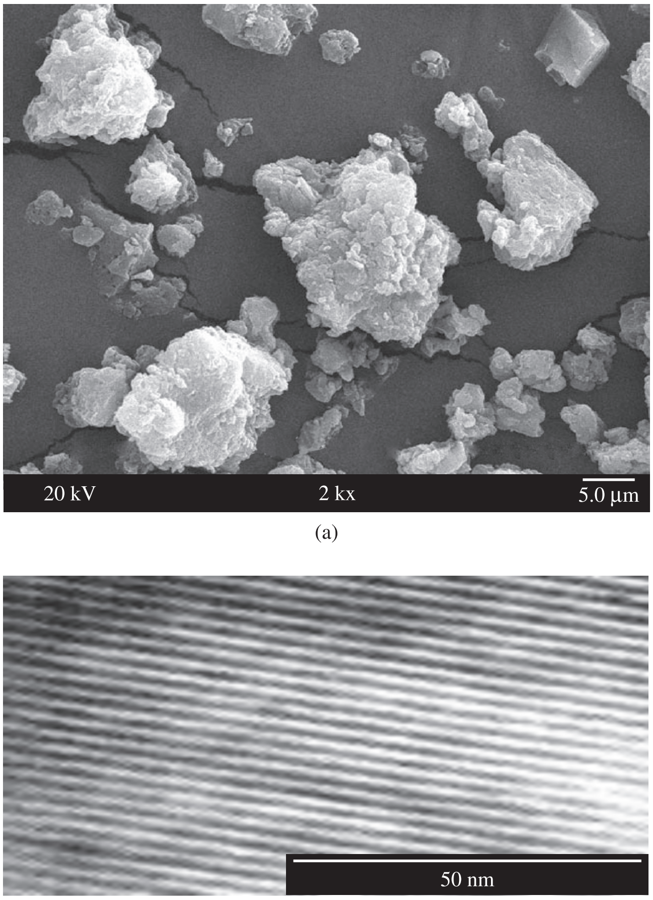


Figure 1. Low angle X-ray diffraction pattern of mesoporous Mn – organophosphate molecular sieve.



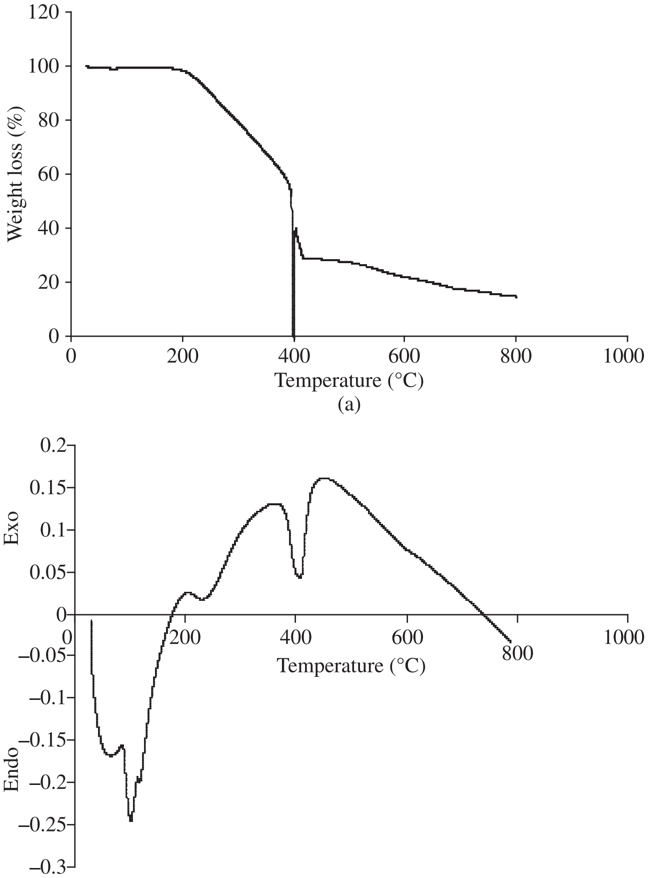
(a)

(b)

Figure 2. a) Scanning electron micrograph and b) Transmission electron micrograph of mesoporous Mn – organophosphate molecular sieve.

however the shape is almost similar (flag shape). It is not soluble in aqueous or non-aqueous media. Presence of manganese plays a major role in it. Transmission electron micrograph of mesoporous Mn – organophosphate (Figure 2b) shows a regular fringe. The well define fringe also shows its crystallinity.

The Thermogravimetry/Differential thermal analysis of mesoporous Mn – organophosphate (Figure 3) losses the total weight exothermically at 25-750 °C (80%). Unlike pure organophosphate (Figure is not shown) the Mn containing organophosphate losses the total weight at lower temperature. It may be due to the metal catalyses the oxidative decomposition of organics.



(a)

(b)

Figure 3. Thermogravimetry (a)/Differential thermal analysis (b) curves of mesoporous Mn – organophosphate molecular sieve.

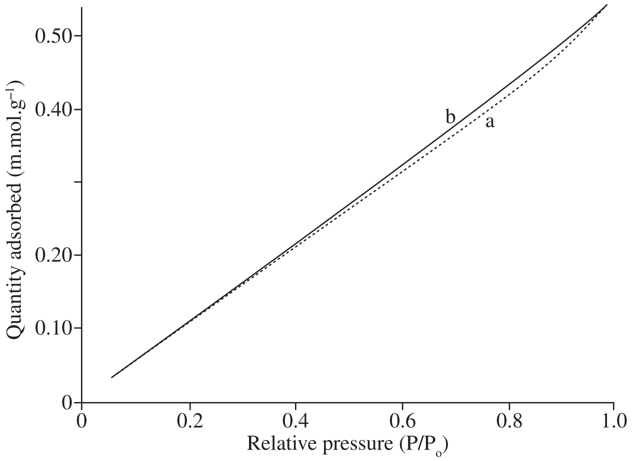


Figure 4. Nitrogen adsorption isotherm curves of mesoporous Mn – organophosphate molecular sieve.

The Nitrogen adsorption isotherms of Mn – organophosphate is of type III[40] (Figure 4). The surface area is 300 m^2/g and pore width is 40 A^o. These results were taken after the materials were activated at 100 °C before measurement. If the material was activated at room temperature, no adsorption was taken place. Normally molecular sieves are activated at 400 °C in vacuum to remove the volatile impurities. The X-ray diffraction pattern of mesoporous Mn-organophosphate

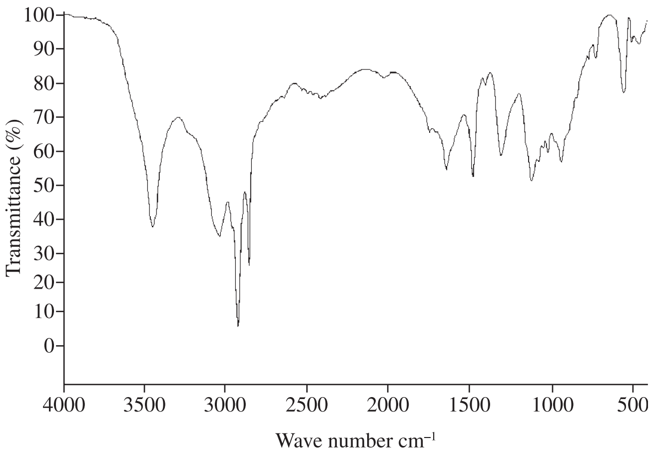


Figure 5. Fourier transform infrared spectrum of mesoporous Mn – organophosphate molecular sieve.

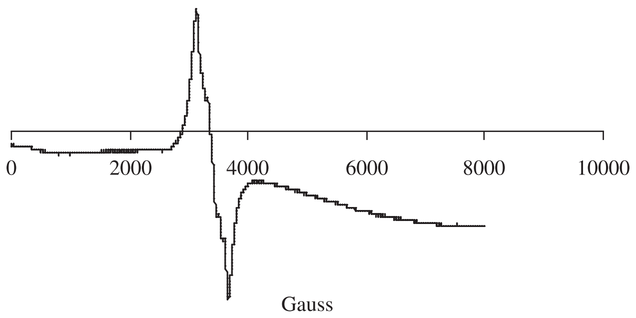


Figure 6. Electron spin resonance spectroscopic analysis of mesoporous Mn – organophosphate molecular sieve.

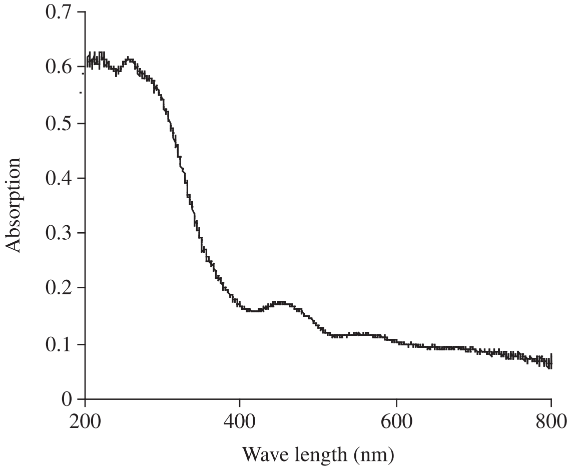


Figure 7. Ultraviolet-visible spectroscopic analysis of mesoporous Mn – organophosphate molecular sieve.

$3CH_3\text{-}(CH_2)_{11}\text{-}NH_2 + P^{5+}O(OH)_3 \rightarrow [(Mn^{3+}(R\text{-}N)\ (R\text{-}N)P^{5+}(O)(N\text{-}R)]_{n-}$
(n-dodecylamine) (orthophosphoric acid) Mn-organophosphate

$+\ Mn^{2+}\ (ac)_2$ $(R = CH_3\text{-}(CH_2)_{11}\text{-})$
(Manganese acetate)

Scheme 1. A plausible mechanism for mesoporous Mn – organophosphate molecular sieve synthesis.

is reproducible even after its thermal treatment up to 200 °C. As we know, the X-ray diffraction reproducibility is essential for better nitrogen adsorption, so we have activated the sample under vacuum at 100 °C.

The Fourier transform infrared spectrum of as-synthesized mesoporous Mn – organophosphate shows (Figure 5) a similar spectrum to other mesoporous molecular sieves. However there are slight changes in intensities. There was peak observed for Mn-O-P vibrations at 960 cm^{-1} band. Electron spin resonance spectrum of mesoporous Mn- organophosphate shows (Figure 6) a single peak for Mn^{3+} oxidation state. It is noted that the Mn^{2+} is having six hyperfine splitting in ESR (I = 5/2)[41]. At liquid nitrogen temperature the peaks intensity is four times higher than the room temperature pattern. Further, even though the source manganese is in Mn^{2+} state, when react with acid it is getting oxidized to Mn^{3+}. Besides for a stable framework, Manganese should be in Mn^{3+}. A week Mn^{2+} hyperfine splitting was also noticed.

Figure 7 shows the Ultraviolet - visible spectra of mesoporous Mn - organophosphate. There is a small peak at 300 nm is due to the presence of tetrahedrally co-ordinated Mn or P species[41]. Another peak at 415 nm is due to square pyramidal species. In Mn – organophosphate, only the tetrahedrally co-ordinated manganese is expected. However due to partial hydration, the square pyramidal species is appeared.

Scheme 1 shows a plausible mechanism for mesoporous Mn-organophosphate synthesis. Orthophosphoric acid has three hydroxyl groups. This three hydroxyl can be easily reacting with three amine group. Being a Lewis acid, Mn is reacted with amine (Lewis base). The structural stoichiometry prevents manganese phosphate formation. The similarity of oxygen with nitrogen creates organophosphate structure similar to zeolites. The need for two hydrogen in organic amine supports this proposal. The organophosphate structure is neutral by presence of alternate P^{5+} and P^{3+} ions. The Mn^{3+} ions replace P^{3+} species to form stoichiometric structure.

4. Conclusions

A novel mesoporous Mn – organophosphate was synthesized for the first time. It is characterized by several physicochemical techniques. Small angle X-ray diffraction analysis shows the first peak at 2.5° for mesoporosity· Elemental analysis shows that the composition is $[(C_{12}H_{23}N)_3PO]$[40]Mn. Scanning electron microscopic picture shows the flag morphology with 1-15 μm particle size. Thermogravimetry/ Differentaial thermal analysis shows almost 80% exothermic weight loss. Nitrogen adsorption isotherm shows it is of type III with 300 m^2.g^{-1}. surface area. Fourier transform Infrared spectroscopic analysis shows that the framework vibrations are comparable to other well known silica mesoporous materials. Electron spin resonance spectroscopic analysis shows the absence of hyperfine splitting indicates the presence of Mn^{3+} species. Ultraviolet – visible spectroscopic analysis shows the most of Mn is in tetrahedral co-ordination beside small square pyramidal species. A plausible mechanism of the reaction was also proposed.

Acknowledgements

One of the authors N.V thanks The Head, Department of Chemistry, National Institute of Technology, Warangal 506 004, Andhra Pradesh, India for constant encouragement through out the work.

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