



# Synthesis of lacunary polyoxometalate encapsulated into hexagonal mesoporous silica and their catalytic performance in esterification



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## ABSTRACT

The lacunary polyoxometalate (LPOM) encapsulated into the hexagonal mesoporous silica matrix materials were successfully prepared via a directly synthesis method by adjusting pH of the preparation system from 2.0 to 6.0. The materials were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, N<sub>2</sub> adsorption–desorption measurements, scanning electron microscopy, X-ray fluorescence analysis, and high-resolution transmission electron microscopy. The results show that the samples possess an ordered pore structure with which changed from uniform ribbing-type to cobweb shape cavity along with the LPOM content increasing from 0% to 30%. The materials possess a high specific surface area of 878–626 m<sup>2</sup> g<sup>-1</sup> and a mesopore diameter of about 3.8 nm. They also show an excellent catalytic performance and a good reusability for the esterification of *n*-butanol with acetic acid.

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## 1. Introduction

Polyoxometalates (POMs) are a large class of metal-oxygen anions and present a large variety of composition, structure and electronic properties which makes them remarkable materials for applications in various areas including catalysis, chemical analysis, medicine or materials science. The majority of the applications of POMs seem to be in the area of catalysis [1], and more research works are focused on the development of homogeneous and heterogeneous catalytic systems with POMs [2–6]. The disadvantages of the homogeneous systems are the difficult to separate the catalyst and products and their poor reusability. For overcoming these problems, many research works have been done to immobilize POMs on appropriate supports such as silicas, activated carbons, zeolites, aluminas, zirconia and titania [7–14]. Mesoporous silicas are the most in common use as the supports. Rana et al. [15] synthesized a Keggin-type Cs salt of Fe substituted mono lacunary phosphotungstate supported MCM-41 by impregnation method. The material showed an amazing catalytic activity and good selectivity on bromination of phenol and on oxidation of trans-stilbene using hydrogen peroxide oxidant. Zheng et al. [16] reported a micro reaction–controlled phase-transfer catalyst. They used a surfactant POM compound [C<sub>16</sub>H<sub>33</sub>(CH<sub>3</sub>)<sub>2</sub>NOH]<sub>3</sub>[PO<sub>4</sub>[WO(O<sub>2</sub>)<sub>2</sub>]<sub>4</sub>] to encapsulate in the channels of silica to compose a micro reaction–controlled phase-transfer system for efficient oxidative desul-

furization. Dibenzothiophene can be oxidized efficiently at mild conditions with S-conversion near 100% on the material. Maksimchuk et al. [17] prepared a catalyst of cobalt-substituted POM supported on amino-modified mesoporous silicates (SBA-15, MCF, and SiO<sub>2</sub>-xerogel). The catalysts can be used repeatedly without loss of the activity and selectivity during several catalytic cycles. Co-oxidation of  $\alpha$ -pinene and isobutyraldehyde produces selectively  $\alpha$ -pinene epoxide with up to 94% selectivity at 96% alkene conversion. Chen et al. [18] reported an efficient heterogeneous catalyst based on highly dispersed Na<sub>7</sub>H<sub>2</sub>LaW<sub>10</sub>O<sub>36</sub>·32H<sub>2</sub>O nanoparticles on mesoporous silica for deep oxide desulfurization. The sulfur removal can be achieved almost 100%. Karimi and Mahjoub [19] provided a novel mesoporous POM hybrid catalyst for heterogeneous oxidation of thioethers. They synthesized K<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> and K<sub>14</sub>[NaP<sub>5</sub>W<sub>30</sub>O<sub>110</sub>] and immobilized them within MCM-48, SBA-3, SBA-15 and NH<sub>3</sub> functionalized mesoporous silicas. They found that the silica frameworks have indispensable effect on oxidation efficiency, stability, and reusability of catalysts. Zhao et al. [20] published a POM-based ionic complex immobilized in mesoporous silica SBA-15 by one-pot procedure for efficient and reusable catalyst for H<sub>2</sub>O<sub>2</sub>-mediated alcohol oxidations in aqueous media. The catalyst showed better catalytic efficiency and reusability than the analog prepared by a multistep process due to better dispersion of the Keggin units, higher structural stability, and lower leaching level of active Keggin units. Estrada et al. [21] gave a series of silica supported transition metal substituted POMs as heterogeneous catalysts in oxidative transformations with hydrogen

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peroxide. Some of these novel heterogeneous catalysts could be reused several times without appreciable loss of catalytic activity.

The hexagonal mesoporous silica (HMS) usually possesses mesoporous structure with a thick wall (2–3 nm) and a good thermal stability. The specific surface area of HMS can be compared beauty with MCM-41, but the pore diameter is usually larger than that of MCM-41 and some other molecular sieves. HMS is more appropriate for using as catalyst or catalyst support for the big molecule reactions. In recent years, HMS materials have been studied for using as supports of heteropolyacids (HPA) [22–26]. The loading method of HPA on HMS is primarily the impregnation method. Benadj et al. [27] used the method to incorporate Keggin-type phosphovanadomolybdic acid ( $H_4PMo_{11}VO_{40}$ ) into HMS material to prepare a catalyst. In the wet impregnation catalyst, the polyoxometalate was highly dispersed in HMS, and possessed a good thermal stability. The catalyst exhibited higher catalytic activity for the reaction of the selective oxidation of propylene by molecular oxygen in the temperature range 200–400 °C, and better selectivity for acrolein, acetaldehyde and acetic acid than that of pure  $H_4PMo_{11}VO_{40}$  which resulted in generation of more  $CO_x$ .

However, the impregnation method has a lot of problems, for example, the large POM molecule is difficult to enter the pore structure of the carriers, which may cause deposition of POM molecules on the external surface of the carriers and result in blocking the channels of the carriers and then reduce the catalytic performance [28–31]. The most serious problem is that the loaded active ingredients can easily dissolve in the polar medium and leach from HMS, which will result in their catalytic performance decreasing in a great degree. Therefore, it is essential to design new synthetic methods for overcoming these disadvantages.

In this work, a direct method for incorporating the lacunary polyoxometalate (LPOM) into HMS to prepare LPOM–HMS hybrid catalysts was designed. For comparison, the sample with same LPOM loading on HMS was also prepared by the wet impregnation method. The catalytic performance of the products was tested by esterification of *n*-butanol with acetic acid as a probe reaction. The results show that the directly synthesized samples possess regular mesoporous structure and exhibit an excellent catalytic performance.

## 2. Experimental section

### 2.1. Materials

Dodecylamine (DDA, A. R.), sodium tungstate dihydrate (A. R.), phosphotungstic acid (HPW, A. R.), dibasic sodium phosphate (A. R., Beijing Jin Yi Fine Chemical Product Company, P. R China), anhydrous ethanol (99.5%), concentrated hydrochloric acid (36 wt.%), tetraethyl orthosilicate (TEOS, A. R., Beijing Chemical Factory, P. R China) were used. All solvents and reactants were commercially available and used without further purification.

### 2.2. Preparation

Amount of 1.54 g of DDA was dissolved in a mixture of 60 mL of deionized water and 20 mL of ethanol under stirring, and the pH was adjusted to 2.0 by adding concentrated hydrochloric acid. Subsequently, a certain amount of HPW aqueous solution was added under continuous stirring. After the solution was clear, 7.5 mL of TEOS was added dropwise into the mixture and stirred for 4 h, and then the pH was adjusted to 6.0 by adding  $NH_4OH$  solution ( $1 \text{ mol L}^{-1}$ ). The mixture was continuously stirred for 12 h at ambient temperature and then heated at 40 °C for 36 h. After crystallization, the product was collected by filtration, washed with deionized water, and dried in an oven at 100 °C for 6 h. The dried

material was calcined at 400 °C for 6 h. The resulting material is denoted *x*% LPOM–HMS, where *x*% is the percentage weight of LPOM. In this paper, 10%, 20% and 30% LPOM–HMS samples were prepared, respectively.

For comparison, the sample of 30 wt.% loading of LPOM on HMS was prepared by using the traditional impregnating method. HMS was synthesized by the reported method [32]. A given amount of HMS was dispersed in 25 mL of ethanol, and then the pH was adjusted to 2.0 by concentrated hydrochloric acid. Afterward, the calculated amount of LPOM [33,34] was dissolved in a small amount of  $CH_3CN$  and added in the above dispersed system and stirred for 3 h at 50 °C. The final mixture was evaporated at 50 °C for 20 h in air and then calcined at 400 °C for 6 h. The sample was designated 30% LPOM/HMS.

### 2.3. Characterizations

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2500 VBZ+/PC diffractometer using  $Cu-K\alpha$  radiation ( $\lambda = 0.1541 \text{ nm}$ ) over the  $2\theta$  range of low-angle 0.5–10° and wide-angle range 5–70°, respectively.

X-ray fluorescence analysis (XRF) was performed on a Philips Magix-601 X-ray fluorescence spectrometer, using  $W-L\alpha$  radiation ( $2\theta = 43.0024^\circ$ , Crystal LiF200, duplex detector, 150 collimator, 60 kV and 60 mA, Al(200  $\mu\text{m}$ ) filter, detection time 40 ms),  $P-K\alpha$  radiation ( $2\theta = 141.0322^\circ$ , Crystal Ge111, flow detector, 550 collimator, 30 kV and 120 mA, no filter, detection time 40 ms) and  $Si-K\alpha$  radiation ( $2\theta = 109.1732^\circ$ , Crystal PE002, flow detector, 550 collimator, 30 kV and 120 mA, no filter, detection time 50 ms) for measuring W, P and Si, respectively. The samples were ground for 300 mesh and pressed pellets at 30 MPa before measurement.

Fourier transform infrared (FT-IR) spectra were obtained in KBr pellets using a Bruker VECTOR 22 spectrometer in the range 400–4000  $\text{cm}^{-1}$ , and all spectra were collected at room temperature with a resolution of 4  $\text{cm}^{-1}$ .

The high-resolution transmission electron microscopy (HRTEM) images were taken using a JEM-3010 with an accelerating voltage of 200 kV.

The nitrogen adsorption–desorption isotherms were obtained using a Quantachrome Autosorb-1 physical adsorption apparatus. Before the nitrogen adsorption, the materials were pretreated in vacuum at 300 °C for 16 h for degassing. The specific surface area ( $S_{BET}$ ) was estimated using Brunauer–Emmett–Teller (BET) equation. The pore size distribution and the mesopore analysis were obtained from the desorption branch of the isotherm using Barrett–Joyner–Halenda (BJH) method [31,35,36].

The acid properties of the samples were determined by  $NH_3$  temperature programmed desorption ( $NH_3$ -TPD) on a TP-5080 Chemical Sorption instrument. About 0.1 g of the sample was placed inside a quartz 'U' tube and pretreated at 400 °C for 1 h in He gas flow of 20 mL/min. The sample was then cooled to 100 °C and was exposed to ammonia at this temperature for 0.5 h, and subsequently was purged with helium for 1 h. The  $NH_3$ -TPD spectrum was recorded between 100 and 750 °C using a temperature ramp of 10 °C  $\text{min}^{-1}$  by monitoring the desorbed ammonia.

### 2.4. Catalytic performance test

The esterification of acetic acid with *n*-butanol was carried out in a three-neck round-bottom flask equipped with a reflux condenser and a water segregator using LPOM–HMS and LPOM/HMS as catalyst, respectively. Amount of 0.20 g of catalyst was added in the mixture of 75 mmol of acetic acid and 25 mmol of *n*-butanol and stirred for 5 h at 115 °C. Then the mixture was cooled to room temperature and a liquid–solid biphasic system was obtained. The

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