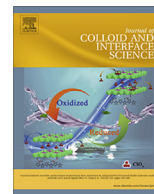




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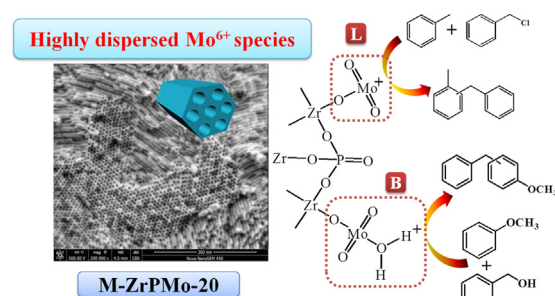
# An efficient ordered mesoporous molybdate-zirconium oxophosphate solid acid catalyst with homogeneously dispersed active sites: Synthesis, characterization and application

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## GRAPHICAL ABSTRACT



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## ABSTRACT

Ordered mesoporous molybdate-zirconium oxophosphate (M-ZrPMo) solid acid catalysts with controllable molybdenum contents (0–20%) are designed and synthesized through a one-pot evaporation-induced self-assembly strategy. Afterwards, ordered mesostructure and molybdenum species in the materials are systematically researched by a variety of means. The results show that M-ZrPMo has highly ordered mesoporous structure with large specific surface area ( $\sim 200 \text{ m}^2 \cdot \text{g}^{-1}$ ), big pore volume ( $\sim 0.30 \text{ cm}^3 \cdot \text{g}^{-1}$ ) and pore size ( $\sim 6.5 \text{ nm}$ ). Additionally, ordered mesoporous structure of M-ZrPMo can be efficiently preserved even treated at  $700^\circ\text{C}$ , presenting an outstanding thermal stability. Meanwhile, the molybdenum species are introduced as designed and homogeneously dispersed in mesoporous framework even at molybdenum content up to 20%. More importantly, the Brønsted and Lewis acidic properties of these materials are successfully enhanced with the introduction of molybdenum species. Meantime, the M-ZrPMo is employed as a solid acid catalyst for alkylation of aromatic compounds and esterification of levulinic acid with 1-butanol. The effect of molybdenum contents and calcination temperature on catalytic performance is thoroughly discussed. The excellent activity and reusability suggested that M-ZrPMo is a promising solid acid catalyst.

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## 1. Introduction

Acid-catalyzed reactions (e.g. alkylation, isomerization, esterification and dehydration) are extensively utilized in modern industry [1–6]. For example, Friedel-Crafts (FC) alkylation reaction is a

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commonly used method for synthesizing diarylalkanes in organic chemistry [7,8]. Esterification of levulinic acid (LA) with 1-butanol (1-BuOH) to butyl levulinate is a significant reaction in the fields of fuels and chemicals [9,10]. Meanwhile, LA is an alternative renewable energy resource and can be gotten from hydrolysis of renewable cellulosic materials. Traditionally, the homogeneous liquid acid catalysts (e.g. HF, H<sub>2</sub>SO<sub>4</sub> and HCl) with high dangerousness and corrosivity are largely used in these reactions. By contrast, heterogeneous solid acid catalysts exist as different phase to reactants and products, and they are easier to be separated and recovered [11,12]. Therefore, solid acid catalyst with high catalytic performance has great potential in acid-catalyzed reactions [13,14].

In regard of heterogeneous solid acid catalyst, the amount of catalytic surface becomes a critical factor defining the number and availability of active sites [15,16]. Ordered mesoporous catalyst has drawn increasing attention in acid-catalyzed reactions due to their large surface areas and pore volumes, strengthened catalytic activity and thermal stability [17–19]. Meanwhile, in compared with the traditional catalysts, their most conspicuous advantage is the possibility to interact with molecules not only at external surface but also within large internal surface. Moreover, the inherent regularity of pore structure in ordered mesoporous materials can decrease the molecular transport limitations, thus allowing molecules to contact with active sites in internal surface of material [20].

In addition, the dispersion of active sites also plays an essential role in catalytic performance. The catalyst with homogeneously dispersed active sites might generate excellent catalytic performance. More importantly, non-uniform distribution of active sites might cause hot spots within the reactor. Therefore, the ordered mesoporous solid acid catalysts with homogeneously dispersed active sites have potential to be deeply investigated. Evaporation-induced self-assembly (EISA) strategy is widely used for synthesizing ordered mesoporous materials [21–24]. In this route, the use of non-aqueous solvents could efficiently slow down the hydrolysis and condensation rate of precursors, which is strongly beneficial for forming ordered mesostructure and obtaining homogeneously dispersed active sites in the mesoporous skeleton.

Metal phosphate is an important type of solid acid catalyst due to its excellent thermal stability, water tolerant ability and easy sedimentation properties [25–27]. In the current years, mesoporous metal phosphate with enhanced activity showed great attention in catalytic fields [28–31]. Mesoporous ZrPO synthesized through a hydrothermal method was reported and exhibited high catalytic activity towards acid catalyzed reactions [30]. Mesoporous tin phosphate was applied for synthesis of 5-HMF from carbohydrates [32]. Ordered mesoporous aluminum-tungstophosphoric acid composites showed high catalytic activity towards isopropanol conversion [33]. In our previous work, M-ZrPO and M-ZrPW solid acid catalysts were synthesized and used for ketalization reaction and FC alkylation reaction [34,35].

In this work, we aim at synthesizing ordered mesoporous molybdate-zirconium oxophosphate (M-ZrPMo) solid acid catalysts with homogeneously dispersed active sites. Small-angle X-ray diffraction (SXRD), N<sub>2</sub> adsorption and desorption isotherms, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) techniques are used to investigate ordered mesostructure and thermostability of materials. Meanwhile, the existing states of introduced molybdenum species in the materials are studied by wide-angle X-ray diffraction (WXR), Raman spectra, X-ray photoelectron spectroscopy (XPS) and H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) characterizations. The acidic properties of materials are researched by temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD) and infrared

spectra of adsorbed pyridine (Pyridine-IR spectra) characterizations. The synthesized M-ZrPMo materials are utilized as solid acid catalysts for alkylation of aromatic compounds which proceeds on Brønsted or Lewis acid sites and esterification of LA with 1-BuOH. In addition, the influences of mesoporous structure and molybdenum species on catalytic activity are intensively discussed. Also, M-ZrPMo is taken five runs to research the stability and reusability of M-ZrPMo in these reactions.

## 2. Experimental section

### 2.1. Synthesis of M-ZrPMo materials

M-ZrPMo was synthesized via a facile one-pot EISA strategy, in which the F127 ((EO)<sub>106</sub>(PO)<sub>70</sub>(EO)<sub>106</sub> triblock copolymer, M<sub>av</sub> = 12600, Sigma-Aldrich) was used as structure-directing agents (SDAs). Typically, F127 (1.2 g) was thoroughly dissolved in anhydrous ethanol (15 mL) by forming a transparent solution. Various precursors (5 mmol of ZrOCl<sub>2</sub>·8H<sub>2</sub>O (zirconyl chloride octahydrate, Sinopharm Chemical Reagent Co. Ltd.), 3.75 mmol of PO(OCH<sub>3</sub>)<sub>3</sub> (trimethyl phosphate, Sinopharm Chemical Reagent Co. Ltd.) and different amounts of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (ammonium molybdate, Sinopharm Chemical Reagent Co. Ltd.)) were added in sequence with vigorous stirring into the above transparent solution and stirred for 6 h. Afterwards, the mixed solution was transferred into a petri dish followed by placed in a drying oven and kept at 60 °C for 48 h and 100 °C for 24 h to undergo the EISA process. The SDAs in the obtained xerogel were removed by calcination at 500 °C for 5 h (with increasing temperature 1 °C·min<sup>-1</sup>). The obtained M-ZrPMo without SDAs was defined as M-ZrPMo-X, where X stood for the molar ratios of Mo/Zr (X = 0, 5, 10, 15, 20). To further investigate the thermal stability of material, M-ZrPMo-20 treated at 600–900 °C was named as M-ZrPMo-20-Y, where Y stood for the final calcination temperature. For example, M-ZrPMo-20-700 referred to the sample M-ZrPMo-20 calcined at 700 °C for 5 h in air atmosphere.

With the purpose of investigating the effect of ordered mesoporous structure on improving catalytic performance, ZrPMo material without introducing F127 was prepared as above-mentioned method and denoted as ZrPMo-20-noF127. Furthermore, the ZrPMo was synthesized via the sol-gel method [36] (ZrPMo<sub>sol-gel</sub>-20) and the contents of Zr, P and Mo species were consistent with M-ZrPMo-20.

### 2.2. Characterization

Thermogravimetric-differential scanning calorimetry (TG-DSC) was performed on NETZSCH STA 449C analyzer with 10 °C·min<sup>-1</sup> to 1000 °C under air atmosphere. Fourier transform infrared spectra (FT-IR) were measured on Nicolet Nexus 870 from 4000 to 400 cm<sup>-1</sup>. XRD was carried out on X'Pert Pro Multipurpose diffractometer (PANalytical, Inc.) using Cu K $\alpha$  radiation (0.15406 nm) source in 2 $\theta$  range from 0.6 to 5.0° (small-angle) and 10.0 to 80.0° (wide-angle). The nitrogen adsorption-desorption isotherms were obtained on ASAP 2020 (Micromeritics Instrument) static volumetric analyzer. The samples were treated at 200 °C for 2 h under vacuum before measurement. The specific surface area was calculated via Brunauer-Emmett-Teller (BET) method and the pore volume was estimated from the amount of nitrogen adsorbed at P/P<sub>0</sub> of 0.990. Pore size distribution (PSD) was obtained by analyzing the adsorption branch of isotherms using Barrett-Joyner-Halenda (BJH) method. High-resolution transmission electron microscopy (FEI TECNAI G<sup>2</sup> F20) with accelerating voltage of 200 kV was taken for TEM images, selected area electron diffraction (SAED), energy-dispersive X-ray spectroscopy (EDS) and elemental mapping tests.

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