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Well-dispersed sulfated mesoporous WO_3/SiO_2 hybrid colloidal spheres: High-efficiency catalysts for the synthesis of fatty acid alkyl esters

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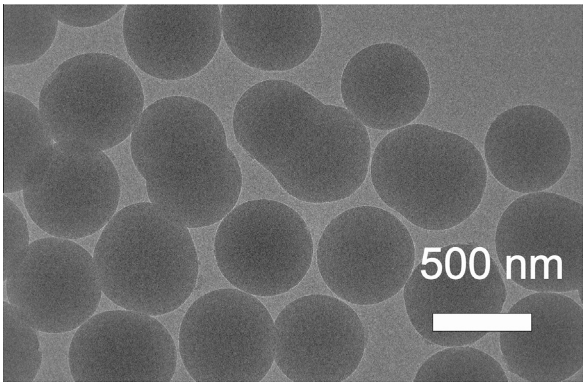
HIGHLIGHTS

- Mesoporous WO_3/SiO_2 spheres with a specific surface area 1370 m^2/g^{-1} were prepared.
- The kinetics-controlled formation mechanism of the colloidal spheres was proposed.
- The sulfated mesoporous WO_3/SiO_2 spheres exhibit excellent catalytic performance.

GRAPHICAL ABSTRACT

We demonstrate an efficient synthesis of well-dispersed mesoporous WO_3/SiO_2 colloidal spheres (WMWCSs) with hexadecyltrimethyl ammonium phosphotungstic (W-6) as precursor and hexadecyltrimethyl ammonium bromide (CTAB) as template. The resulted WO_3/SiO_2 colloidal spheres exhibit a high specific surface area of 1370 $m^2\,g^{-1}$ and pore volume of 0.84 $cm^3\,g^{-1}$ with pore size of 2.44 nm. The formation mechanism as-prepared WMWCSs was also proposed. Treated with sulfuric acid, the sulfated mesoporous WO_3/SiO_2 hybrid colloidal spheres (SWMWCSs) were obtained, and the SWMWCSs exhibited excellent catalytic performance in the synthesis of biodiesel *via* the esterification of long-chain free fatty acids (FFAs).



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ABSTRACT

An effective method in obtaining well-dispersed mesoporous WO_3/SiO_2 colloidal spheres (WMWCSs) with a specific surface area of 1370 $m^2\,g^{-1}$, pore volume of 0.84 $cm^3\,g^{-1}$, and pore size of 2.44 nm was developed. This method allows easy control over the morphology, size and dispersity of the hybrid spheres by the variation of synthetic conditions. The formation mechanism on the as-prepared WMWCSs was proposed as well. Treated with sulfuric acid, the resulted WO_3/SiO_2 colloidal spheres exhibited excellent catalytic activity in the synthesis of biodiesel *via* the esterification of long-chain free fatty acids (FFAs). A 96.9% conversion of oleic acid was realized under optimized conditions, 3 wt% of catalyst and 6 h of reaction time, while the catalyst suffered no obvious loss in activity for five consecutive runs.

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1. Introduction

The use of biodiesel is of great interest during the past decade due to diminishing petroleum reserves and environmental concerns [1]. Homogeneous basic catalysts, such as potassium hydroxide, sodium hydroxide or alkoxides are usually used for the production of biodiesel in industrial scale owing to higher reaction rate compared with acid-catalyzed reaction. However, the use of these base catalysts lead to serious contamination problems that require the implementation of tedious washing and separating processes [2]. Besides, they are sensitive to FFAs and water present in the reactants [3]. Some of these problems can be avoided with the use of heterogeneous acid catalyst since they are reusable, separated easily from the reaction mixture and active in the formation of high purity products due to the elimination of washing process [4]. Several solid acid catalysts have been prepared and used for the preparation of biodiesel, including sulfated zirconia [5], $SO_4^{2-}/SnO_2–SiO_2$ [6], and WO_3/MCM-41 [7].

Colloidal multicomponent hybrid materials with tunable composition and morphology have recently been subjected to extensive research because of their potential applications in diverse areas such as catalysis, solar energy conversion, and optoelectronic devices [8]. For better mass transportation of the reaction species, mesoporous multicomponent hybrid nanomaterials are usually preferred [9]. Such porous structure can provide channels for the reaction species to reach the surface of the nanoparticles where the catalytic reaction occurs. The catalytic activity of mesoporous multicomponent hybrid materials for certain reactions (such as CO oxidation) may be enhanced when the particle size is down to the nanoscale [10]. Up to date, there have been two main strategies for the preparation of the mesoporous materials. One resorts to templating reagents, the other is based on metal–organic frameworks (MOFs) constructed from molecular building blocks [11]. However, highly efficient fabrication strategies in producing mesoporous multicomponent hybrid colloidal spheres remain challenging.

Among transition metal oxides, tungsten oxide in various nanostructure morphologies has afforded great potential in a wide range of applications, which include heterogeneous catalysts, chromogenic devices, solar-energy devices, and field electron emission [12–16]. Although various hierarchical WO_3 structures with different morphologies have been synthesized by a variety of methods in recent years [13–18], with regard to the synthesis of mesoporous multicomponent hybrid colloidal spheres composed of WO_3 and other oxides, however, the research is scarce. In this presentation, the WMWCSs were prepared with hexadecyltrimethyl ammonium phosphotungstic (W-6) as precursor and hexadecyltrimethyl ammonium bromide (CTAB) as template. Treated with sulfuric acid, the sulfated mesoporous WO_3/SiO_2 hybrid colloidal spheres (SWMWCSs) were obtained, and the SWMWCSs exhibited excellent catalytic performance in the synthesis of biodiesel *via* the esterification of FFAs.

2. Experimental

2.1. Chemicals and materials

Phosphotungstic acid (HPW) with principal composition of $H_3PO_4{\cdot}12WO_3{\cdot}xH_2O$ was obtained from J&K Chemical. CTAB was provided by Aladdin Reagent Company. Tetraethylorthosilicate (TEOS), oleic acid (OA), palmitic acid, lauric acid, methanol, ethanol, propanol and butanol were purchased from Chemical Reagent Company of China. All the reagents were used as received.

2.2. Synthesis of W-6

W-6 was obtained simply by the reaction of HPW and CTAB in absolute ethanol (Eq. (1)). Typically, CTAB (0.44 g) was dissolved in absolute ethanol (100 mL). To this clear solution, HPW (1.15 g) dissolved in absolute ethanol (50 mL) was added dropwise from a burette with vigorous stirring. The resultant precipitate was washed three times with absolute ethanol and dried at 60 °C for 24 h.

$$3\left[C_{16}H_{33}N(CH_3)_3\right]Br + H_3PW_{12}O_{40}\cdot xH_2O \rightarrow \left[C_{16}H_{33}N(CH_3)_3\right]_3PW_{12}O_{40}\downarrow + 3HBr + xH_2O \tag{1}$$

2.3. Preparation of the WMWCSs

Typically, W-6 (200 mg) and absolute ethanol (20 mL) were transfered to a round-bottom flask. After sonication for 15 min, H_2O (80 mL) was added to the above suspension. The mixture was stirred at 28 °C for 6 h before concentrated ammonia solution (28 wt.%, 0.30 mL) was added. After stirring for 30 min, 0.60 mL of TEOS was slowly added dropwise and maintained at 28 °C for 16 h with vigorous stirring. The obtained samples were washed with deionized water and ethanol several times. Finally, the product was calcined at 450 °C for 4.5 h.

2.4. Preparation of the SWMWCSs

The SWMWCSs were obtained by impregnating the WMWCSs (50 mg) into H_2SO_4 of different concentrations. The mixture was then dried at 100 °C followed by calcination at 450 °C for 3 h to form the SWMWCSs denoted as SWMWCSs-X. SWMWCSs-0.5, 0.75, 1.0, and 1.5, meaning that 50 mg of the WMWCSs was treated by 20 mL of H_2SO_4 solution of 0.5, 0.75, 1.0, and 1.5 M, respectively.

2.5. Characterization

The specific surface area and pore structure were determined by N_2 adsorption–desorption at −196°°C using a Micromeritics ASA 2420 analyzer. The size and morphology of the products were characterized by transmission electron microscopy (TEM, JEOL JEM-2011) and scanning electron microscopy (SEM, JEOL-6701F). X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/max 2550P C diffractometer (Rigaku, Japan). Fourier transform infrared (FTIR) spectra were recorded on a Bruker Tensor 27 instrument. FTIR of pyridine adsorbed on SWMWCSs to characterize the acid sites of the catalysts was conducted using a Nicolet 6700 FTIR spectrometer at a resolution of 4 cm^{-1}. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al-Kα radiation. The base pressure was about 3×10^{-9} mbar. X-ray fluorescence (XRF) analysis was carried out in a PANalytical PW2403 spectrometer.

2.6. Typical catalytic reaction procedure

Typically, a three-neck glass flask equipped with a reflux condenser was charged with OA (0.6 g), methanol (2.72 g) and an appropriate amount of fresh catalyst. The mixture was refluxed for 4 h with vigorous stirring in a silicone oil bath. Then the heating was stopped and the flask was left to cool down to room temperature. After the esterification was complete, the used solid catalyst samples were separated from the reaction mixture by ‘low speed’ filtration and were collected for reusability tests. Before reusing they were dried at 100 °C for 1 h. The percent of conversion of OA into its ester was estimated by measuring the acid value of the product by titration with sodium hydroxide. The conversion of OA was calculated by formula (2):

$$x\% = \frac{a_i - a_t}{a_i} \times 100 \tag{2}$$