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A study of the catalytic behavior of phosphotungstic acid-modified Janus particles in a heterogeneous oil/water pickering emulsion system

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ABSTRACT

An emulsion interface materialization method was used to obtain amphiphilic silica Janus nanoparticles. Reducing the photosynthesis of aquatic organisms after water pollution. $PW_{12}O_{40}^{3-}$ was introduced onto Janus particles by ion exchange, and an amphiphilic particle emulsion catalyst (PWO-J) was prepared. Hydrogen peroxide was used as the oxygen source, and the amphiphilicty of the catalyst was used to assemble the catalyst at the Pickering emulsion interface. The PWO-J catalyst was found to exhibit very high catalytic activity toward the oxidation of oleic acid in water-in-oil systems. The results showed that PWO-J catalysis of oxidation had similar results as CTAB and phosphotungstic acid (control system) under the same conditions. The azelaic acid recovery rate was 86.7%, and PWO-J could be reused 4 times. A reaction mechanism was proposed, and the constructed model was used to calculate a reaction rate constant of $15.32 \times 10^{-5} L \cdot mol^{-1} \cdot s^{-1}$ for the PWO-J system. The PWO-J system had a lower activation energy than the control system, showing that the catalytic oxidation of oleic acid into azelaic acid was more likely to occur in the PWO-J system.

1. Introduction

Selective oxidation of oleic acid into azelaic acid is an important reaction in heterogeneous systems. With the growing demand for dioctyl azelate (DOZ) plasticizers, cosmetics, fragrances, and other products, this reaction has become a popular topic of research [1–4]. In this reaction, using H_2O_2 as the oxidizing agent [4] in the oxidation of oleic acid allows a single-step reaction [2] without any solid byproducts to be achieved. Oakley et al. [3] used 30% hydrogen peroxide in *tert*-butanol solvent with tungstic acid as a catalyst to oxidize oleic acid into dihydroxy compounds which were then oxidized into azelaic acid. Antonelli et al. [5] reported the use of 40% hydrogen peroxide with $[(n\text{-}C_8H_{17})_3NCH_3]_3\text{-}\{PO_4[W(O)(O_2)_2]_4\}$ as a catalyst and quaternary ammonium salt as a phase transfer catalyst to oxidize oleic acid into azelaic acid with 79% selectivity.

Although the yield of azelaic acid in the above studies was relatively high, H_2O_2 oxidation of oleic acid is a heterogeneous reaction, and water-soluble oxidizing agents and catalysts require the use of surfactants to form microemulsions in order to increase the contact rate with the hydrophobic substrate (oleic acid). Thus, facile and effective product isolation and catalyst recovery can avoid the urgent unsolved problem of environmental surfactant contamination and creating H_2O_2 after reaction.

Solid particles stabilized emulsions [6], which are usually mentioned as "Pickering emulsions", have attracted much attention during the last decades [7], as many drawbacks of emulsions stabilized by conventional surfactants could be avoided [8]. Pickering emulsion systems are formed by solid nanoparticles instead of traditional surfactants at the surface of the dispersed phase, forming a thin film that effectively blocks droplets from coalescing [9]. This yields a stable oil/water dispersed phase (PE emulsion) that not only ensures full contact between the oil and water phases but also facilitates product isolation and catalyst recovery, making it a two-phase reaction system with great potential. Janus particles are a type of amphiphilic particle [10–13] that increases the stability of the emulsion while also modifying its end groups [11–14], yielding emulsion-catalysis dual function.

In this study, phosphotungstic acid-modified amphiphilic Janus particles were used as emulsion-catalysts and recovered for reuse after reaction termination by centrifugation. The function and mechanism of emulsion catalysis is emphasized, expanding the application of Janus materials to PE emulsion catalysis in heterogeneous reactions.

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2. Experimental

2.1. Materials

Analytical grade phosphotungstic acid, hydrogen peroxide, oleic acid, cetyltrimethylammonium bromide (CTAB), sorbitan monostearate (Span-60), polyoxyethylene sorbitan monostearate (Tween-60), dioctadecyldimethylammonium chloride (DODMAC), and other substances were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

AVATAR370 infrared spectrometer, Nicolet, USA; WRS-1B digital melting-point apparatus, Shanghai Precision Science Instrument Co., Ltd.; ADVANCEAV 500 MHz NMR spectrometer, Bruker, Switzerland; Agilent 8453 UV–visible spectrophotometer, Macy Instrument, Ltd.; GWF-8JD particle analyzer, Tianjin Tianhe Analytic Instrument Co., Ltd., measurement range 3–3000 nm.

2.2. Experimental methods

2.2.1. Preparation of heteropoly acid-modified Janus particles

Based on reports in the literature [15,16], Janus nanoparticles with amino groups on one side and phenyl groups on the other side were obtained through an emulsion interface materialization method. Specifically, 1 g dry powdered polydivinylbenzene/polystyrene hollow particles were dispersed in 20 g of water and stirred at 70 °C to form the seed emulsion. Next, 0.6 g of [3-(methacryloyloxy)-propyl]trimethoxysilane, 0.6 g of 1.0 wt% potassium persulfate, and 0.02 g sodium dodecylbenzenesulfonate were dispersed in 10 g of water and sonicated for 2 min at room temperature to form the monomer emulsion. Next, the monomer emulsion was slowly dropped into the seed emulsion at 70 °C within 30 min, and the mixture was allowed to stand for polymerization for different times. After polymerization, a quantity of NH_3•H_2O (28 wt%) was added at 70 °C with stirring and allowed to react for 1 h to initiate further polydivinylbenzene sol-gel processes.

20 mg snowman-shaped composite particles were collected and dispersed in 20 mL deionized water, and 60 mg $H_3PW_{12}O_{40}$ was added to the dispersion. After reaction at room temperature for 1 h with magnetic stirring, the mixture was centrifuged and washed 3 times with deionized water, after which snowman-shaped composite Janus particles with $PW_{12}O_{40}{}^{3-}$ negative ions (hereafter abbreviated PWO-J) were obtained.

2.2.2. Catalytic oxidation of oleic acid

PWO-J system: 100 g oleic acid and a certain mass of PWO-J were added to a three-necked flask reactor equipped with a magnetic stirrer, a thermostat, and a reflux condenser, mixed thoroughly, stirred, and heated to 50 °C. H_2O_2 began to be dropped into the mixture, and the temperature was increased as H_2O_2 was dropped. H_2O_2 dropping ended within 2 h, and the mixture was allowed to react at 70 °C for 8 h.

Control system: The same amount of phosphotungstic acid and its corresponding phase-transfer catalyst (CTAB) as the amount of $PW_{12}O_{40}{}^{3-}$ in the PWO-J system was added; other reaction conditions are the same as described above.

2.2.3. Recovery of Janus particles

After reaction termination, the emulsion was placed in a centrifuge for centrifugal isolation. The Janus particles were isolated, washed with water, ethanol, chloroform, and other solvents, purified, and recovered for reuse.

2.2.4. Azelaic acid separation and purification

After termination of the catalytic oxidation of oleic acid, the residual liquid separated into a light yellow organic layer and a translucent aqueous layer. A quantity of boiling water was used to extract the oil several times until no azelaic acid crystals were present in the extract. After cooling at room temperature, white azelaic acid flakes were obtained by filtration [17,18].

2.3. Method of hydrophile-lipophile Balance(HLB) value determination

The HLB value of the PWO-J emulsifier was determined using trial and error [16]. An aqueous emulsifier solution prepared from 25 mL deionized water and 5 g mixed emulsifier (Span and Tween, Span and PWO-J) was used to emulsify 20 g of oleic acid at 35 °C to form an O/W emulsion. Under the same conditions, emulsification experiments were performed (emulsification for 30 min by dropping of the oil phase into the aqueous emulsifier solution with electric stirring) through continuous adjustment of the proportion of emulsifier used, and the efficiencies of the emulsifier in each experiment were compared.

3. Results and discussion

3.1. Structural characterization of substances

3.1.1. Structural characterization of amphiphilic catalysts

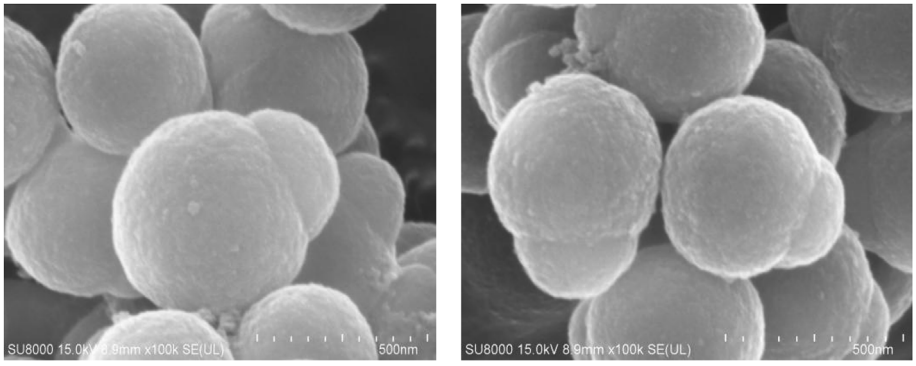
PWO-J has a hydrophobic phenyl group and a hydrophilic $[PW_{12}O_{40}]^{3-}$ group and is an amphiphilic catalyst that tends to be enriched at the water/oil interface and has surface activity as a result.

SEM images of snowman-shaped composite Janus particles before and after phosphotungstic acid loading are shown in Fig. 1.

It can be seen from Fig. 1 that the composite Janus particles have a snowman-like shape, uniform size, smooth surface, and a particle size of approximately 500 nm. After loading, the particle size and shape were generally consistent.

Particle size analysis results are shown in Fig. 2.

It can be seen from Fig. 2 that the difference in particle size before



(a) before loading (b) after loading

Fig. 1. SEM images of snowman-shaped composite Janus particles before and after phosphotungstic acid loading.