

A Study of the Catalytic Behavior of Phosphotungstic Acid-Modified Janus Particles in a Heterogeneous 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. $\text{PW}_{12}\text{O}_{40}^{3-}$ 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 amphiphilicity 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. 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.

Index Terms—janus particles; pickering emulsion; heterogeneous catalysis; isolation; recovery; aquatic organisms

I. INTRODUCTION

The selective oxidation of oleic acid to azelaic acid is an important reaction in heterogeneous system [1]. With the increasing demand for DOZ plasticizers and cosmetics perfumes worldwide, this reaction has become a current research hotspot [2]. One step reaction and no solid by-product can be achieved by oxidizing oleic acid with H_2O_2 as oxidant. Oakley et al. [3] used tungstic acid as catalyst, oxidized oleic acid with 30% hydrogen peroxide in solvent tert-butanol to obtain dihydroxy compounds and then oxidized to azelaic acid. Although the yield of azelaic acid obtained by the above study is relatively high, the reaction of H_2O_2 oleic acid is heterogeneous. The water-soluble oxidants and catalysts need to form microemulsion with surfactant to enhance the contact rate with hydrophobic substrates (oleic acid) [4]. Therefore, how to separate products and recover catalysts simply and efficiently while avoiding environmental pollution caused by surfactants after reaction has become an urgent problem to be solved in the heterogeneous system of hydrogen peroxide oxidation.

The Pickering emulsion system uses solid nanoparticles instead of traditional surfactants to form thin films on the surface of dispersed droplets, effectively preventing the aggregation between droplets and obtaining stable oil/water dispersive phase (PE emulsion). It can not only ensure full contact between oil-water phases, but also facilitate the separation and recovery of products and catalysts. Therefore, it is a potential two-phase reaction system. As a amphiphilic particle [5], Janus particles can improve the stability of the emulsion while modifying the end group, and get the dual function of emulsification and catalysis [6].

In this study, the amphiphilic Janus particles modified by phosphotungstic acid were used as emulsifying catalysts. After the reaction, they were reused by centrifugation. The effect and mechanism of emulsion catalysis were discussed, and the application of Janus materials in the PE emulsion catalysis in heterogeneous reactions was extended.

II. EXPERIMENTAL SECTION

A. Reagents and Instruments

Phosphotungstic acid, hydrogen peroxide, oleic acid, cetyltrimethylammonium bromide (CTAB), sorbitol anhydride monostearate (Span-60), sorbitol monostearate polyoxyethylene ether (Tween-60) and octadecyl dimethyl ammonium chloride (DODMAC) are all analytical purities, which are provided by Shanghai Pharmaceutical Reagents Company.

AVATAR370 Infrared Spectrometer, Nicolet Company, USA; WRS-1B Digital Melting Point Instrument, Shanghai Precision Scientific Instrument Co., Ltd; ADVANCEAV500MHz Nuclear Magnetic Resonance Instrument, Bruker Company, Switzerland; Agilent 8453 Ultraviolet-Visible Spectrophotometer, Shanghai Metro Analysis Co., Ltd; GWF-8JD Particle Analyser, Tianjin Tianhe Analytical Instrument Co., Ltd., measuring range is 3-3000 nm.

B. Experimental Method

According to [5] report, Janus nanoparticles with one side of amino group and phenyl group on the other side were obtained by emulsion interface material method. The 20 mg snowman-shaped composite particles were

dispersed in 20 mL deionized water and 60 mg H3PW12O40 was added into the dispersing solution. Janus Snowman composite particles (PWO-J) with PW12O403- were obtained by centrifuging the mixture and washing it with deionized water three times after reaction at room temperature for 1 hour under magnetic stirring.

PWO-J system: 100g oleic acid and PWO-J of a certain quality were added into a three-port bottle reactor with magnetic stirrer, constant temperature controller and reflux condensation tube. The mixture was uniform, stirred, heated to 50 °C, and then dripped with H2O2 and heated at the same time. The hydrogen peroxide was dripped within 2 hours and reacted at 70 °C for 8 hours.

Contrast system: The same amount of phosphotungstic acid and corresponding phase transfer reagent (CTAB) were added to PW12O403- in PWO-J system, and other reaction conditions were the same.

After the reaction is finished, the emulsion is centrifuged and centrifugally separated. The Janus particles are separated and washed, purified, recovered and prepared for reuse again with ice water, ethanol and chloroform.

After the catalytic oxidation of oleic acid, the remaining liquid is divided into yellowish oil layer and transparent water layer. The oil is extracted many times with a certain amount of boiling water until the extract does not crystallize azelaic acid. The white flake-like azelaic acid is filtered after cooling at room temperature.

III. RESULTS AND DISCUSSIONS

A. Characterization of the Structure of Azelaic Acid

The NMR spectra of the product are shown in Figure 1.

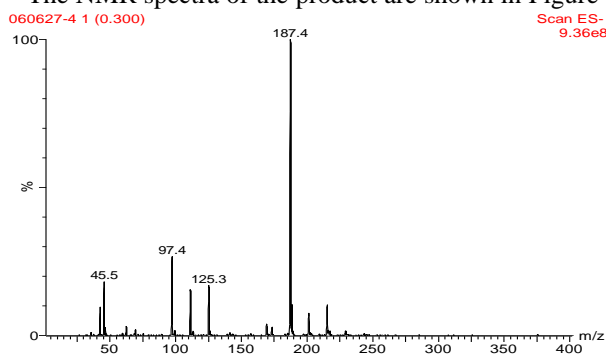


Figure 1. Mass spectra of the synthesized product.

From the chemical shift, splitting characteristics and integral area of the absorption peaks, the existence forms of methyl and carboxyl groups in the products can be identified. Among them, 10.74 (b2, 2H) broad peak is the active H on two carboxyl groups; 2.35 (t, 4H) triple peak, 4 H; 1.63 (m, 4H) multiple peak, 4 H; 1.34 (m, 6H) multiple peak, 6 H, which conforms to the molecular structure of azelaic acid and confirms that the products are azelaic acid.

B. Structural characterization of amphiphilic catalysts

PWO-J has phenyl group and $[PW_{12}O_{40}]^{3-}$ (hydrophilic group). It is an amphiphilic catalyst. It tends to enrich at the water/oil interface and thus has surface activity.

The element contents before and after ion exchange were analyzed by EDX, as shown in Table 1. After ion exchange, the contents of P and W were 0.58 wt% and 3.05 wt% respectively.

Table 1. The elemental content in Janus particles before and after ion exchange.

Element	Mass fraction /%	
	Before exchange	After exchange
CK	63.93	60.20
NK	3.63	3.50
OK	24.37	26.99
SiK	5.46	5.66
WM	0	3.05
PK	0	0.58

C. Effect of Reaction Conditions on Conversion Rate

The catalytic reaction of emulsion occurs on the water/oil interface of emulsion droplets. Therefore, the stirring speed has an important influence on the formation of emulsion and the oxidation reaction. The effect of stirring speed on the oxidation of oleic acid in emulsion system at 90 °C was investigated. As shown in Figure 2, stirring speed strongly affects the oxidation of oleic acid. The conversion of oleic acid is 60% in 60 minutes at 500 rpm, 76% at 1000 rpm, 88% at 2000 rpm, and almost unchanged at 3000 rpm. It is worth noting that the conversion of oleic acid is reversed when stirring speed increases to 4000 rpm. It dropped to 83%. That is to say, the oxidation rate of oleic acid increases first and then decreases with the increase of stirring speed. The stirring speed changed the properties of the emulsion and affected the oxidation rate of oleic acid.

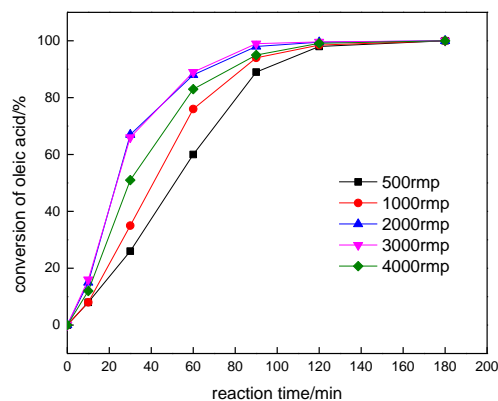


Figure 2. Conversion of oleic acid the reaction time in emulsion at different mixing speed.

C. Phase Transfer Reagent

The preparation of azelaic acid by oxidation of oleic acid is a heterogeneous reaction, and phase transfer reagent is needed. The reaction of CTAB, PWO-J and Span-60 with phosphotungstic acid as catalyst was

compared. The results are shown in Table 2. When PWO-J was used as phase transfer reagent, phosphotungstic acid was not added.

Table 2. Influence of different phase transfer reagents on conversion.

Phase transfer reagent	HLB value	Conversion rate /%
Span-60	4.7	75
CTAB	15.6	100
PWO-J	12.52	100

From Table 2, it can be seen that the catalytic systems consisting of PWO-J and CTAB as phase transfer reagents have high catalytic oxidation activity, and the conversion rate is 100%, while the conversion rate is only 75% when Span-60 is used as phase transfer reagent. For oil-water two-phase reaction, water soluble catalyst phosphotungstic acid must be able to enter the oil phase and oleic acid reaction to increase the conversion of oleic acid. The HLB value of emulsified oil acid is 17 [10]. The HLB values of CTAB and PWO-J are both close to 17. The emulsification effect is good, the conversion rate is high, and the HLB value of Span-60 is much less than 10. Therefore, W/O emulsion cannot be formed, so the conversion rate is low.

IV. CONCLUDINGINGS

The amphiphilic emulsifying catalyst (PWO-J) was synthesized by emulsion interface material method and ion exchange method. By using the amphiphilic nature, oleic acid was formed in the Pickering emulsion catalytic oxidation system in hydrogen peroxide solution. The emulsion based catalytic system not only increases the reaction interface, but also avoids the loss of catalyst and oxidant, which improves the catalytic efficiency and reduces the cost. With PWO-J as catalyst, the yield of azelaic acid remained above 84% after 4 times reuse. It is inferred that the reaction between catalytic intermediates and epoxides occurs mainly at the oil phase and the two phase interface. Thermodynamic and kinetic models show that the reaction is endothermic, and the system is low in chaos and is not easy to epoxidation. It needs external forces to promote the reaction. The activation energy of the PWO-J system is less than that of the contrast system, which indicates that the catalytic oxidation of oleic acid to azelaic acid is more likely to occur in the PWO-J system.

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