



A simple strategy towards the preparation of a highly active bifunctionalized catalyst for the deacetalization reaction

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ABSTRACT

A bifunctional catalyst containing both the hydrophobic methyl and hydrophilic sulfonic acid groups has been successfully fabricated by mild surface modification of the pre-prepared silica nanoparticles. To its credit, the methyl groups in the catalyst were applied to improve the surface wettability of silica solid nanoparticles, while the sulfonic acid groups were devoted to catalyzing the deacetalization of various acetal derivatives. The catalyst was characterized in detail by Scanning electron microscope (SEM), Transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FT-IR) and Thermogravimetric analysis (TGA). The catalytic results revealed that the bifunctional SiO₂-Me&SO₃H NPs exhibited superior activity for the deacetalization of 4-methoxybenzaldehyde dimethyl acetal and the product conversion could be >99% within 45 min in the toluene/water biphasic system. The main reason was probably due to the formation of Pickering emulsion, which could greatly improve the interface area between the oil and water and decrease the mass transfer resistance

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1. Introduction

Pickering emulsions (solid particles-stabilized emulsions) are colloidal emulsions that are stabilized by solid particles instead of traditional surfactant molecules [1,2]. In principle, the solid particles with appropriate hydrophilicity/hydrophobicity (wettability) can be strongly adsorbed at the interface between two immiscible fluids such as oil and water, creating an effective steric/electrostatic shield for the emulsified droplets [3–5]. And in terms of the wettability of the solid particles, the Pickering emulsion can be classified into either oil-in-water (O/W) or water-in-oil (W/O) type of emulsion. Generally, the hydrophilic particles tend to form O/W emulsion, while the hydrophobic particles prefer to generate W/O emulsion [6,7]. Beyond that, these solid particles-stabilized emulsions also offer unique advantages over traditional surfactant including reduced foaming, strong kinetic hindrance to droplet coalescence and tunable interfacial permeability. More recently, the researchers have demonstrated that the Pickering emulsions hold great promise in a variety of potential applications ranging from

food production, cosmetics, coating and catalysis to petroleum industries [8–12].

Particularly, the intense research has been fueled by the development of Pickering emulsion catalyst for alcohol oxidation [13], alkene epoxidation [14], nitroarenes hydrogenation [15,16] and biofuel upgrade reactions [17–20]. Among them, the solid nanoparticles-stabilized emulsion catalytic system, in which the solid nanoparticles serve as both emulsifiers and catalysts, has proven superior to traditional surfactant-stabilized emulsion due to its easy separation and high recyclability [21,22]. To date, various solid particles including SiO₂ NPs, Fe₃O₄ NPs, TiO₂ NPs, zeolites, carbon nanotubes (CNTs) as well as their composites with appropriate wettability can be well located at the interface between the oil/water two phase [23–28]. Moreover, after immobilizing the catalytically active species onto the above support surface, they are likely to seat at the amphiphilic catalyst-stabilized Pickering emulsion droplet interface. In this regard, the resulting plentiful micro-size nanoreactors not only greatly increase the oil/water biphasic contact area but also substantially reduce the transfer resistance of organic substrates and avoid the self-aggregation and leaching of catalytic active sites during the reaction [29].

The integration of amphiphilic solid nanomaterials and metal nanoparticles has been a fruitful area in hydrogenation [30], oxidation [31], biomass conversion [32] and esterification reactions

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[33]. These studies proved that the solid catalyst materials with amphiphilic properties can not only significantly accelerate the reaction rate but also optimize the product selectivity to a certain extent. The possible reason was that they could greatly improve adsorption of substrates on the catalytic activity sites at the oil–water biphasic interfaces and exclude the product from the catalyst surface simultaneously. But as far as we know, the amphiphilic metal-free solid nanoparticles for the heterogeneous catalytic reaction in oil–water biphasic systems are still rarely reported [34]. In the current work, we present a simple strategy towards the preparation of a highly active metal-free bifunctionalized catalyst for the deacetalization reaction. The catalyst was prepared via the simultaneous modification of the silica nanoparticles surface with the hydrophobic methyl and hydrophilic sulfonic acid organosilanes. The deacetalization results demonstrated that the amphiphilic $\text{SiO}_2\text{—Me}\&\text{SO}_3\text{H}$ catalyst possessed excellent catalytic activity and stability in toluene/water biphasic system.

2. Experimental

2.1. Materials and methods

2-(4-Chlorosulfonylphenyl) ethyltrichlorosilane in methylene chloride (CSPETS) was purchased from J&K Co., Ltd. Methyltrichlorosilane (MTCS), tetraethyl orthosilicate (TEOS) and aqueous ammonia (25 wt%) were purchased from Aladdin Chemical Reagent Co., Ltd. All other chemicals and reagents were analytical grade and used without further purification. Deionized water was used in the whole experiment.

2.2. Preparation of the solid silica nanoparticles (SiO_2 NPs)

The SiO_2 NPs were synthesized by the classical Stöber method and with slight modification. Typically, 20 mL of aqueous ammonia (25 wt%) was added into the mixture of 400 mL of ethanol and 50 mL of deionized water via ultrasonication. After vigorously stirring for 30 min, 20 mL of TEOS was added slowly, and the mixture was stirred for another 6 h to obtain the uniform silica nanoparticles. The resulting products were recovered through centrifugation and washed several times with deionized water and ethanol, and then dried at 50 °C under vacuum for 12 h.

2.3. Preparation of methyl and sulfonic acid bifunctionalized SiO_2 NPs ($\text{SiO}_2\text{—Me}\&\text{SO}_3\text{NPs}$)

The synthesis of $\text{SiO}_2\text{—Me}\&\text{SO}_3\text{H}$ NPs was based on the condensation of 2-(4-chlorosulfonylphenyl) ethyltrichlorosilane (CSPETS) and methyltrichlorosilane (MTCS) in the presence of the silica nanoparticles, which was based on our previously reported work [35]. In a typical procedure, 1.0 g of SiO_2 NPs were dispersed into 50 mL of dry toluene via ultrasonication, then MTCS (0.4 mL, 3.0 mmol) and CSPETS (0.25 mL, 0.5 mmol) were slowly added into above mixture. The resulting mixture was stirred for 24 h at room temperature, and then it was washed three times with ethanol and each time was 15 mL. Subsequently, the solid samples were suspended in 1 M H_2SO_4 (50 mL) solution for 4 h, washed with a large amount of deionized water and dried at 50 °C under vacuum for 12 h to give the corresponding $\text{SiO}_2\text{—Me}\&\text{SO}_3\text{H}$ NPs. Elemental analysis result of the as-prepared catalyst revealed that the content of carbon, hydrogen and sulfur was 4.05 wt%, 1.69 wt% and 0.45 wt%, respectively.

2.4. Determination of the $\text{SiO}_2\text{—Me}\&\text{SO}_3$ catalyst's acidity

The concentration of sulfonic acid groups was determined by ion-exchange pH analysis protocol [36]. Typically, 50 mg of

$\text{SiO}_2\text{—Me}\&\text{SO}_3\text{H}$ catalyst was added to a 25 mL of 1.0 M NaCl aqueous solution, and the resulting suspension was stirred at room temperature for 48 h until equilibrium was reached. The filtrate was titrated with 50 mM NaOH and phenolphthalein was applied as indicator. The acid amount of $\text{SiO}_2\text{—Me}\&\text{SO}_3\text{H}$ catalyst was determined to be 0.14 mmol g^{-1} , which was highly consistent with the elemental analysis result.

2.5. General procedure for the hydrolysis reaction of acetal derivatives

The hydrolysis reaction of acetal derivatives was performed in a 10 mL of round bottom flask. A typical reaction process was as follows: 45 mg of $\text{SiO}_2\text{—Me}\&\text{SO}_3\text{H}$ NPs (6.3 μmol of $\text{—SO}_3\text{H}$ groups) was put into the reactor, 3.0 mL of toluene and 3.0 mL of deionized water were added as solvent. After stirring for 5 min, 1 mmol of benzaldehyde dimethyl acetal was added into above mixture by syringe. The hydrolysis reaction was carried out at 30 °C for 45 min. After the reaction, the product was obtained through centrifugation and then the supernatant was determined by Agilent 7890A GC. Then the catalyst was recovered and washed several times with deionized water and ethyl acetate, dried at 50 °C for 2 h, and subsequently used in the next cycles.

3. Results and discussion

The morphology and structure of SiO_2 NPs and $\text{SiO}_2\text{—Me}\&\text{SO}_3\text{H}$ NPs were firstly elucidated by SEM. The representative SEM images of the as-prepared SiO_2 NPs and $\text{SiO}_2\text{—Me}\&\text{SO}_3\text{H}$ NPs are shown in Fig. 1a and b, the low magnification SEM image illustrated the large-scale formation of uniform monodisperse spherical SiO_2 NPs and $\text{SiO}_2\text{—Me}\&\text{SO}_3\text{H}$ NPs with an average diameter of ~ 150 nm. The TEM image (Fig. 1c and d) showed that the $\text{SiO}_2\text{—Me}\&\text{SO}_3\text{H}$ NPs have a rough surface compared with the pure SiO_2 NPs, indicating that each nanosphere consists of SiO_2 and $\text{—Me}\&\text{SO}_3\text{H}$ organic silane and the presence of $\text{—Me}\&\text{SO}_3\text{H}$ affected the morphology of SiO_2 , which was consistent with the FT-IR results.

Fig. 2 shows the digital photographs and optical microscopy images of $\text{SiO}_2\text{—Me}\&\text{SO}_3\text{H}$ NPs-stabilized Pickering emulsions. The formation process of Pickering emulsions was as follows: 30 mg of $\text{SiO}_2\text{—Me}\&\text{SO}_3\text{H}$ NPs, 3 mL of toluene and 3 mL of water were added into a 10 mL of glass vial. The mixture was sonicated for 2 min and then violently stirring for another 5 min, and then standing for 1 h for optical microscope analysis. As can be seen in Fig. 2a, the whole materials were participated into the production of the emulsion and the height of the emulsion layer was about 0.95 cm, while the height of the upper toluene was approximately 0.44 cm. Thus, it can be speculated that the emulsification efficiency reached up to 68%. As for Fig. 2b, the optical microscopy image revealed that the $\text{SiO}_2\text{—Me}\&\text{SO}_3\text{H}$ NPs-stabilized Pickering emulsions with ellipsoidal shape and the droplets size were below 300 μm , which were well-dispersed on the glass slide. More importantly, the obtained emulsion could greatly improve the interface area between the oil and water and decreased the mass transfer resistance.

FT-IR spectroscopy was employed to verify the successful modification of $\text{—Me}\&\text{SO}_3\text{H}$ groups on the as-synthesized SiO_2 NPs. As shown in Fig. 3a, FT-IR spectra of the SiO_2 NPs around 1110 cm^{-1} and 795 cm^{-1} corresponded to the antisymmetric and symmetric stretching vibrations of Si—O—Si bond in oxygen–silica tetrahedral, respectively. The presence of the anchored alkyl groups was confirmed by the aliphatic weak C—H stretching vibrations appearing at 2975 cm^{-1} and 2884 cm^{-1} in the $\text{SiO}_2\text{—Me}\&\text{SO}_3\text{H}$ NPs. An increased intensity and broadening of the band at 3000–3500 cm^{-1} in the samples suggested the existence of more —OH groups on the $\text{SiO}_2\text{—Me}\&\text{SO}_3\text{H}$ NPs. Taken together, these results indicated

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