



Ionic liquid-Pluronic P123 mixed micelle stabilized water-soluble Ni nanoparticles for catalytic hydrogenation



Yinyin Yu^a, Wenwen Zhu^a, Li Hua^a, Hanmin Yang^b, Yunxiang Qiao^a, Ran Zhang^a, Li Guo^a, Xiuge Zhao^a, Zhenshan Hou^{a,*}

^a Key Laboratory for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science and Technology, 200237 Shanghai, China

^b Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission and Ministry of Education, Hubei Province, South-Central University for Nationalities, 430074 Wuhan, China

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ABSTRACT

Ionic liquid (1-butyl-2,3-dimethylimidazolium acetate, [BMMIm]OAc)-Pluronic P123 mixed micelle stabilized water-soluble Ni nanoparticles were characterized by UV-vis, XRD, XPS and TEM and then employed for catalytic hydrogenation. It was demonstrated that the mixed-micelle stabilized Ni NPs showed excellent catalytic performance for the selective hydrogenation of C=C and nitro compounds in the aqueous phase under very mild reaction conditions, and also the Ni NPs catalysts can be recycled at least for eight times without significant decrease in catalytic activity. The results of characterization revealed that the mixed micelle-stabilized Ni NPs catalysts were highly dispersed in aqueous phases even after five catalytic cycles. In addition, adding ionic liquid ([BMMIm]OAc) can affect the micelle structure of P123 solutions and thus afford an additional steric protection from aggregation of Ni NPs, resulting in enhancing stability and catalytic activity of Ni NPs.

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1. Introduction

The development of transition metal nanoparticle (NPs)-catalyzed hydrogenation reactions has been intensively pursued because they can produce high-value products in fine chemicals, pharmaceuticals and perfume manufacture [1–3]. Both the catalytic activity and the selectivity were found to be strongly influenced by the size, morphology and composition of the metal NPs [4–6]. However, because metal NPs are thermodynamically unstable and agglomerated easily, they were normally stabilized by means of either electrostatic or steric protection to achieve high turnover numbers in catalytic reactions. Hence, surfactants, ionic liquids, polymers, dendrimers, polyoxoanions and ligands have been utilized to stabilize the metal NPs through the interaction of stabilizing reagents with the metal NPs surface [7–10]. The stabilizing metal NPs such as Pd, Pt, Rh, Ru and Ni excellent catalytic activities in hydrogenation for unsaturated double bonds [10–13].

Traditionally, hydrogenation reaction was performed in organic solvents. As an alternative solvent, water is a more favorable reaction solvent, in comparison with conventional organic solvents. Because it is non-flammable, non-toxic, and offers the easy approach for separation of organic reagents from catalysts which were immobilized in aqueous phase. Therefore, the aqueous phase

hydrogenation reaction has attracted much attention whatever in the homogeneous or heterogeneous reaction [14,15]. However, owing to the weak interaction between the hydrophobic substrates and the catalysts immobilized in aqueous phase, the mass transfer is diffusion-limited, and thus the rate of reaction performed in aqueous phase is too slow for a commercial process [16,17]. In order to circumvent this problem, polymers anchored on the surfaces of the metal NPs, amphiphilic reagents including surfactants, ligands with alkyl chains and quaternized aminoalkyl groups, could be employed to prevent agglomeration of NPs and accelerate the mass transfer rate [18–21]. Through using amphiphilic reagents, significant rate enhancement can be observed because the interaction between substrates and catalysts is increased through the hydrophobic interior of the amphiphilic reagents. For example, polyvinylpyrrolidone (PVP) stabilized Ru NP catalysts have been utilized for aqueous phase hydrogenation reaction, where PVP not only provided hydrophobic microenvironment for the substrate but also prevented aggregation [22]. Moreover, the water-soluble Rh and Pd NPs stabilized with amphiphilic reagents can promote hydrogenation rate with good efficiency in aqueous phase, which further demonstrated the positive role of stabilizing agent [23,24]. Besides, ionic liquids as solvent or additives have also been found to improve the catalytic activity of metal NPs [25,26].

The water soluble poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymers (PEO-PPO-PEO) can

* Corresponding author. Fax: +86 21 64253372.

E-mail address: houzhenshan@ecust.edu.cn (Z. Hou).

coordinate on the particle surface, which make the system solvated by their amphiphilic properties. For these reasons, the stable metal NPs have been synthesized by using PEO–PPO–PEO triblock copolymers as stabilizing agents [27–30]. For example, Au NPs have been synthesized in aqueous PEO–PPO–PEO block copolymer solutions at ambient temperature, and the block copolymers functioned efficiently as both the reductant and the colloidal stabilizer [27–33]. Using CO₂-in-water emulsions, P123 stabilized Pd NPs showed high catalytic activities and selectivities in hydrogenation of citral, and the turnover frequency (TOF) of the reaction was up to 6313 h⁻¹ [28]. Although P123 stabilized Ni and Co NPs also have been prepared and characterized, no reports were concerned on their catalytic performance [34,35].

The cost-effective Ni NPs have attracted significant interests in catalytic applications recently, especially in selectivity hydrogenation reaction. During the 90's of the 20th century, it was found that Raney nickel can be utilized for hydrogenation reactions. However, the conversions and selectivities were not good enough, and Raney nickel's stability was also poor for the industry application. From then on, the Ni NPs had been synthesized by using surfactants, polymers or ionic liquids as stabilizing agents and hydrazine or NaBH₄ as reductant, respectively. The as-prepared Ni NPs showed higher catalytic activities and selectivities than that of Raney nickel [36–38]. Nevertheless, Ni NPs might be not stable in aqueous solution because of the Ni NPs oxidation, leading to the formation of nickel oxide or hydroxide. Hence, there was only few studies that reported the Ni NPs catalyzed hydrogenation reaction in aqueous phase [39–41]. Our group have found that the water-soluble Ni NPs stabilized by amino-functionalized ionic liquids was able to catalyze the aqueous phase hydrogenation efficiently, and the Ni catalysts can be recycled for seven times without significant loss of activities [13,40].

On the basis of the previous work, in this work the ionic liquid-triblock copolymer P123 mixed micelle-stabilized Ni NPs was synthesized successfully and employed for the aqueous phase hydrogenation of olefin and α,β -unsaturated aldehydes. It has been demonstrated that using basic imidazolium ionic liquids as additives could not only improve the activities and selectivities in the hydrogenation reaction, but also facilitate the separation of catalyst form catalytic aqueous phase. Several important factors influencing the catalytic performance of Ni NPs have been discussed, such as kinds of ionic liquids, surfactant concentration, and reaction temperature. The interaction between ionic liquids and the micelle of P123 also had been illustrated.

2. Materials and methods

2.1. Materials

Analytical reagent grade nickel acetate tetrahydrate (Ni(OAc)₂·4H₂O), hydrazine hydrate (N₂H₄·H₂O, 85%), sodium hydroxide (NaOH, 96%), ethanol (EtOH, 99.8%), various substrates and all other materials were purchased from SCRC (Sinopharm Chemical Reagent Co., Ltd., Shanghai). Triblock polymers P123 (P123, PEO₂₀–PPO₇₀–PEO₂₀, *M* = 5750) was purchased from Sigma–Aldrich. Double distilled water was used in all experiments.

2.2. Synthesis of ionic liquids

Ionic liquids used in this work were synthesized according to the procedure described elsewhere. 1-Butyl-2,3-dimethylimidazolium chloride [BMMIm]Cl was prepared and purified by the procedure described in the literature [42,43]. Briefly, the reaction of 1,2-dimethylimidazole with an excess of 1-chlorobutane (1.2 equiv) was performed at 70 °C for 48 h. Then the solid product of

[BMMIm]Cl was washed with ethyl acetate, followed by drying at 60 °C under vacuum for 24 h. [BMMIm]Cl; ¹H NMR(400 MHz, CDCl₃, 25 °C, TMS): δ = 0.97 (t, *J* = 7.3 Hz, 3H, CH₃), 1.38 (m, 2H, CH₂), 1.80 (m, 2H, CH₂), 2.82 (s, 3H, CH₃), 4.01 (s, 3H, CH₃), 4.21 (t, *J* = 7.4 Hz, 2H, CH₂), 7.56 (d, *J* = 1.98 Hz, 1H, CH), 7.83 (d, *J* = 1.98 Hz, 1H, CH).

1-Butyl-3-dimethylimidazolium chloride [BMMIm]Cl was prepared according to the similar procedures as [BMMIM]Cl instead of using N-methylimidazole. [BMMIm]Cl; ¹H NMR(400 MHz, CDCl₃, 25 °C, TMS): δ = 0.96 (t, *J* = 7.3 Hz, 3H, CH₃), 1.40 (m, 2H, CH₂), 1.91 (m, 2H, CH₂), 4.13 (s, 3H, CH₃), 4.31 (t, *J* = 7.3 Hz, 2H, CH₂), 7.41 (d, *J* = 1.98 Hz, 1H, CH), 7.60 (d, *J* = 1.98 Hz, 1H, CH), 10.71 (s, 1H, C2-H).

1-Butyl-2,3-dimethylimidazolium acetate [BMMIm]OAc was prepared by following steps: a mixture of [BMMIm]Cl and NaOAc (1.5 equiv) was dissolved in ethanol (5 ml) and stirred at room temperature (RT) for 72 h. After reaction, the mixture was filtered, and the filtrate was rotary-vacuum evaporated just to dryness at 80 °C. Then colorless or pale yellow viscous liquid [BMMIm]OAc was obtained. The ionic liquids [BMMIm]N(CN)₂, [BMMIm]CF₃COO and [BMMIm]PF₆ were synthesized in a similar method. A mixture of [BMMIm]Cl and the inorganic salt NaN(CN)₂, NaCF₃COO or KPF₆ (1.5 equiv) was dissolved in ethanol (5 ml) and stirred at RT for 72 h. Then the mixture was filtered, the filtrate was rotary-vacuum evaporated just to dryness at 80 °C, and the corresponding ionic liquids were obtained. [BMMIm]OAc: ¹H NMR(400 MHz, D₂O, 25 °C): δ = 0.80 (t, *J* = 7.3 Hz, 3H, CH₃), 1.24 (m, 2 H, CH₂), 1.68 (m, 2 H, CH₂), 1.89 (s, 3H, OAc), 2.44 (s, 3H, CH₃), 3.62 (s, 3 H, N–CH₃), 3.99 (t, *J* = 7.4 Hz, 2 H, CH₂), 7.11 (d, *J* = 2.13 Hz, 1 H, CH), 7.21 (d, *J* = 2.13 Hz, 1 H, CH). [BMMIm]N(CN)₂: ¹H NMR (400 MHz, D₂O, 25 °C): δ = 0.81 (t, *J* = 7.4 Hz, 3H), 1.21 (dq, *J* = 14.8, 7.4 Hz, 2H), 1.67 (dq, *J* = 12.8, 7.5 Hz, 2H), 2.46 (s, 3H), 3.99 (t, *J* = 7.3 Hz, 2H), 7.18 (d, *J* = 2.1 Hz, 1H), 7.22 (d, *J* = 2.1 Hz, 1H). [BMMIm]CF₃COO: ¹H NMR (400 MHz, D₂O, 25 °C): δ = 0.80 (t, *J* = 7.4 Hz, 3H, CH₃), 1.21 (d, *J* = 14.8, 7.4 Hz, 2H, CH₂), 1.66 (d, *J* = 12.8, 7.5 Hz, 2H, CH₂), 3.98 (t, *J* = 7.3 Hz, 2H, CH₂), 7.18 (d, *J* = 2.1 Hz, 1H, CH), 7.22 (d, *J* = 2.1 Hz, 1H, CH). [BMMIm]PF₆: ¹H NMR (400 MHz, D₂O, 25 °C): δ = 0.85 (t, 3H, *J* = 7.4), 1.29 (d, 2H, *J* = 7.4), 1.79 (q, 2H, *J* = 7.4), 3.83 (s, 3H), 4.09 (t, 2H, *J* = 7.4), 7.28 (d, 1H), 7.31 (d, 1H).

2.3. Preparation of Ni NPs catalyst

Anhydrous ethanol (total 5 ml) containing triblock polymers P123 (28 mg, 0.005 mmol) and Ni(OAc)₂·4H₂O (12 mg, 0.05 mmol) were placed in Schlenk flask under an atmosphere of nitrogen. After stirred at RT for 5 h, NaOH (4 mg, 0.1 mmol) was added slowly to the solution, followed by adding hydrazine hydrate (13 mg, 0.25 mmol) as reductant at 70 °C. After 10 min, the solution color changed from green to brownish-black, which indicated the formation of Ni NPs. The mixture was cooled to RT, and then the dialysis membrane (1 KDa molecular weight cut off) was used to remove residual ethanol and base in double distilled water until the pH value was decreased to 7. The resulting Ni NP aqueous solution (about 7 ml) was concentrated to 2 ml, and then stored in flask under N₂ atmosphere for further uses.

2.4. Preparation of Raney nickel catalyst

For the sake of comparison, Raney Ni catalyst was prepared according to a published procedure [44]. In a three necked flask contained 50 ml of a 10% sodium hydroxide solution, 0.2 g Raney nickel aluminum alloy (50%), was added in small portions (20–30 min) with stirring, and the temperature of solution was kept at 90–95 °C during the addition. Then the mixture was stirred for 1 h. The stirring was interrupted, the nickel was allowed to settle, and the solution was decanted. The residue was washed with ten

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