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Selective hydrogenation of furanic aldehydes using Ni nanoparticle catalysts capped with organic molecules

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ABSTRACT

Ni nanoparticles were synthesized by a colloidal method in the presence of organic surface-capping agents and used to catalyze the selective hydrogenation of unsaturated furanic aldehydes to furanic alcohols. The effects of the Ni nanoparticle size and surface organic layer were evaluated. Of the 3.7, 5.1, 6.8, and 10.4 nm Ni nanoparticles tested in selective furfural (FFR) hydrogenation to furfuryl alcohol (FFA), the 6.8 nm Ni nanoparticles exhibited the highest yield because access to the surface sites on the smaller and larger nanoparticles was blocked by the densely packed organic layer and by their agglomeration due to magnetic attraction, respectively. The capped Ni nanoparticles exhibited a high FFA yield of 96%, whereas significant over-hydrogenation was observed when uncapped calcined Ni/SiO_2 catalysts with similarly sized Ni nanoparticles were employed. Steric hindrance of the Ni surface induced by the organic surface layer led to selective FFR hydrogenation to FFA. The capped Ni nanoparticles could be reused repeatedly without a significant loss in the FFA yield. They also exhibited high selectivity (>90%) in the hydrogenation of other unsaturated furanic aldehydes to their corresponding alcohols.

1. Introduction

Producing chemicals from biomass has received much attention because it is more environmentally friendly than producing them from crude oil [1–3]. Various furanic compounds can be derived from lignocellulosic biomass resources and subsequently used to synthesize many valuable chemicals [4,5]. For example, polysaccharide hemicelluloses in biomass undergo hydrolysis when treated with an acid at elevated temperatures to produce sugar molecules. The sugar molecules can be dehydrated to yield furfural (FFR), which can then be converted to furfuryl alcohol (FFA) by catalytic hydrogenation [6,7]. FFA is typically used to produce resins, foundry binders, fibers, lubricants, and fine chemicals such as lysine or vitamin C [8,9]. Recently, the catalytic hydrogenation of unsaturated furanic aldehydes to their corresponding alcohols has been studied extensively [10–14]. Because furanic aldehydes contain both C=C and C=O bonds, the C=O bond should be selectively hydrogenated while the C=C bond is preserved. Cu-Cr alloys with various modifiers have been mainly used for FFR conversion to FFA [15,16]. Bimetallic Pd-Cu [17], Pt-Sn [18], Ni-Sn intermetallic structure [19], Mo-doped Co-B alloys [20], Pt nanoparticles deposited on various supports [21], Co/SBA-15 [22], and Ru/Zr-MOFs [23] have also been reported to have high FFA selectivity in this reaction.

Metallic nanoparticles have been widely used for selective catalytic reactions. They are often synthesized using colloidal methods; the metal precursor is reduced in the presence of organic capping agents, which stabilize the nanoparticles when dispersed in solution by decreasing their high surface energies. The surface-capping agents usually block the surface metal sites, resulting in lower activity. However, some recent studies have shown that organic agents can promote certain surface reactions. Medlin et al. showed that thiolate layers adsorbed on Pt/Al_2O_3 and Pd/Al_2O_3 catalysts enabled the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol and of 1-epoxy-3-butene to 1-epoxybutane [24,25]. Rodionov et al. showed that PtFe alloy nanoparticles with fluorous ligands bound to the Fe surface sites could catalyze cinnamaldehyde hydrogenation to cinnamyl alcohol [26], and Fu et al. showed that this selective hydrogenation reaction could also be catalyzed by Pt_3Co alloy nanocrystals with various amine ligands on the surface [27]. It was proposed that the obtained high selectivity was due to steric hindrance, which caused the reactants to adsorb on the surface sites in a specific adsorption mode.

In some cases, the organic capping agents even increased the catalytic activity. Zheng et al. showed that capping Pt nanowire surfaces with ethylenediamine changed their electronic structure, enabling the electron-rich Pt catalysts to produce *N*-hydroxylanilines from

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nitroaromatics with high activity and selectivity [28]. Miki et al. showed that intermolecular hydrophobic interactions between alkanethiol capping agents on Au nanoparticles and the reactants in silane alcoholysis led to a higher reaction rate [29]. Kunz et al. showed that Pt nanoparticles functionalized with L-proline ligands catalyzed the hydrogenation of acetophenone exclusively to phenyl-1-ethanol with high activity due to the ligand-accelerated hydrogenation of the carbonyl via the N—H effect [30]. Zheng et al. showed that $Au_{34}Ag_{28}$ nanoclusters coated with alkynyl ligands catalyzed hydrolytic triethylsilane oxidation more efficiently than uncapped or partially capped nanoparticles [31].

In this work, capped Ni nanoparticles of various sizes were employed in the selective hydrogenation of unsaturated furanic aldehydes to their corresponding alcohols. The capped Ni nanoparticles, which are much cheaper than precious metal (e.g. Pt and Pd) nanoparticles, could catalyze furanic alcohol production with high selectivity, whereas fully hydrogenated products were obtained when Raney Ni or uncapped Ni nanoparticles were used as the catalyst. The role of the organic layer in the catalytic reaction was investigated.

2. Experimental

2.1. Synthesis of Ni nanoparticle catalysts

Ni nanoparticles of various sizes were prepared by previously reported methods [32,33]. Nickel acetylacetonate ($Ni(acac)_2$; 95%, Sigma-Aldrich), oleylamine (OAm; 70%, Sigma-Aldrich), and trioctylphosphine (TOP; 90%, Sigma-Aldrich) were placed in a 75 mL three-necked round-bottom flask and heated at 120 °C for 20 min in an N_2 atmosphere under stirring to obtain a homogeneous solution. The flask was then heated to 220 °C in 20 min, maintained at this temperature for 2 h, and subsequently cooled to room temperature. The resulting nanoparticles were washed with isopropanol (IPA; 99.5%, Samchun) three times, and redispersed in 11 mL IPA. The 3.7 nm Ni nanoparticles were washed with a 1:1 (v/v) mixture of IPA and ethanol (99.9%, Samchun) three times and redispersed in 11 mL IPA. The specific amounts of the chemicals used to synthesize the different Ni nanoparticles are presented in Table S1. It was previously reported that OAm is the reductant and controls the nucleation rate while TOP provides a tunable surface stabilization through coordination on the Ni surface [34]. As the amount of TOP increased, the size of Ni nanoparticles decreased.

Ni/SiO_2 catalysts with no surface-capping agents and Ni/C catalysts with surface-capping agents were also prepared for comparison. The Ni nanoparticles were sonicated with commercial silica (99.8%, Sigma-Aldrich) for 1 h. The obtained Ni/SiO_2 samples were dried in a convection oven at 80 °C overnight. The dried samples were calcined at 450 °C for 1 h in air to remove the organic surface species and then reduced at the same temperature for 1 h in a 10% H_2 (with N_2 balance) atmosphere. The 6.8 nm Ni nanoparticles were deposited on carbon supports. The Ni nanoparticle solution was sonicated with carbon (Vulcan, XC-72R) for 1 h and then stirred at 700 rpm overnight. The obtained Ni/C sample was washed by centrifugation. The amount of Ni nanoparticles in the Ni/SiO_2 and Ni/C samples was ~10 wt%.

2.2. Characterizations

Transmission electron microscopy (TEM) images were recorded on a Tecnai TF30 ST instrument operated at 300 kV. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analyses were performed on an Agilent ICP-OES 720 instrument to determine the Ni nanoparticle concentration in the IPA solution and the Ni weight percentages in the Ni/SiO_2 and Ni/C samples. The magnetic properties of the Ni nanoparticles were measured by a SQUID-vibrating sample magnetometer (Quantum Design MPMS 3) with a maximum field of 70,000 Oe at 300, 350, and 400 K. Thermogravimetric analysis (TGA) of the powder Ni nanoparticle samples, which were obtained after IPA was completely evaporated overnight in vacuum oven at 80 °C, was performed using a thermogravimetric analyzer (Netzsch, TG 209 F3) under an N_2 atmosphere with a ramping rate of 10 °C/min. The organic content on the Ni nanoparticles was estimated by the weight loss in the range of room temperature to 900 °C. Diffuse reflectance Fourier-transform infrared spectroscopy (DRIFT) measurements were performed using a Nicolet iS-50 (Thermo Scientific). 10 mg of Ni nanoparticles was mixed and grinded with 90 mg of KBr. The mixed powder was put into a sample cup and set into a DRIFT cell. The cell was covered by KBr window. The cell was purged with Ar gas (98 sccm) for 2 h at room temperature. To remove water in the DRIFT cell, the cell was additionally purged with Ar gas at 110 °C for 2 h, and the cell was cooled to room temperature under the Ar flow. Then, 2% CO gas was charged for 20 min at room temperature. The DRIFT spectra were collected under vacuum.

2.3. Hydrogenation reactions

FFR (99%, Sigma-Aldrich) 1 mL and various amounts of the nickel catalysts were added to 30 mL of a solvent (methanol (99.8%, Duksan), ethanol, IPA, or methyl isobutyl ketone (MIBK; 99.5%, TCI)). Raney Ni (Ni 92.5%, TCI) was washed with ethanol and distilled water twice each and dried in a vacuum oven at 50 °C before use. The mixed solution was placed in a 100 mL Teflon liner with a magnetic stir-bar and sealed in a stainless steel autoclave. Then the reactor was purged with H_2 three times to exclude other gases. The autoclave was heated to 110 °C at which temperature the hydrogenation reaction was performed under 30 bar H_2 and stirring at 700 rpm. After the reaction, the autoclave was cooled, and the solution was subsequently centrifuged at 11,000 rpm for 10 min to separate the liquid-phase products from the catalyst. For the recycling tests, 1 mL of FFR and 30 mL of IPA were added to the centrifuged Ni catalyst without any further treatment. The products were analyzed by a gas chromatograph (GC; YL 6100) equipped with a capillary column (DB-624, Agilent Technologies, 30 m × 0.53 mm × 3.00 μm) and flame ionization detector (FID).

The selective hydrogenation of various unsaturated aldehydes and ketones was performed according to the following protocol. The reactant 1 mL (3-cyclohexene-1-carboxaldehyde (97%, Sigma-Aldrich), 5-hydroxymethyl-2-furaldehyde (99%, Sigma-Aldrich), 5-methylfurfural (99%, Sigma-Aldrich), 2-thiophenecarboxaldehyde (98%, Sigma-Aldrich), pyrrole-2-carboxaldehyde (98%, Sigma-Aldrich), 3-furancarboxaldehyde (⩾97%, Sigma-Aldrich), 2-furyl methyl ketone (99%, Sigma-Aldrich), acetophenone (99%, Sigma-Aldrich), cinnamaldehyde (99%, Sigma-Aldrich), or trans-2-hexen-1-al (98%, Sigma-Aldrich)) was added to 30 mL of IPA. The 6.8 nm Ni nanoparticle catalyst (20 mg) was charged to the reactor. The hydrogenation reactions were then performed according to the FFR hydrogenation protocol, except the reaction temperature was 100 °C for 3-cyclohexene-1-carboxaldehyde.

3. Results and discussion

3.1. The property of capped Ni nanoparticles

Different sizes of Ni nanoparticles were synthesized with the size of 3.7 ± 0.4, 5.1 ± 0.4, 6.8 ± 0.8, and 10.4 ± 1.0 nm as shown in