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Chemoselective Transfer Hydrogenation of Nitroarenes Catalyzed by Highly Dispersed, Supported Nickel Nanoparticles

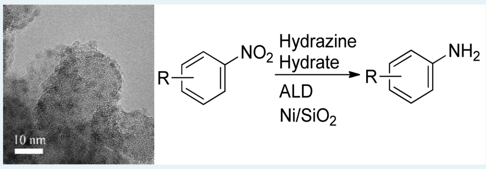
Chengjun Jiang,[†,§] Zeyu Shang,[‡,§] and Xinhua Liang*[,‡]

[†]Department of Chemical and Biological Engineering, Zhejiang University of Science & Technology, Hangzhou, Zhejiang 310023, People's Republic of China

[‡]Department of Chemical and Biochemical Engineering, Missouri University of Science and Technology, Rolla, Missouri 65409, United States

Supporting Information

ABSTRACT: A recyclable highly dispersed Ni/SiO_2 catalyst was prepared by atomic layer deposition. Chemoselective reduction of nitroarenes was studied using the prepared Ni/SiO_2 as the catalyst and hydrazine hydrate as a hydrogen donor. Different kinds of nitroarenes were converted to the corresponding anilines with high yields. The high activity of the catalysts could be a result of the highly dispersed Ni nanoparticles.



KEYWORDS: *atomic layer deposition (ALD), nickel nanoparticles, heterogeneous catalysis, chemoselective, transfer hydrogenation, nitroarenes*

1. INTRODUCTION

Aromatic amines are useful intermediates in the preparation of dyes, pharmaceuticals, and agricultural chemicals, which can be obtained by the reduction of aromatic nitro compounds. A variety of procedures involving metal catalysts and other reducing agents are available for this purpose;[1−4] however, the selective reduction of a nitro group in the presence of other reducible functional groups in a molecule is a challenging task. In addition, reduction of aromatic nitro compounds often stops at an intermediate stage, yielding hydroxylamines, hydrazines, azoarenes, or azoxyarenes as byproducts.[5−7] Recently, many catalysts involving metal nanoparticles (e.g., Au,[8−10] Ag,[11] Fe,[12] Fe−Ni,[13] Ni−B,[14,15] Ru,[16,17] and Pd[18,19]) have been employed for the reduction of nitro groups. Among the catalysts, gold showed the highest activity and selectivity; however, gold is a noble metal and very expensive. Nickel and iron are good reducing agents and much less expensive than gold. Various liquid-phase-based methods were applied to prepare Ni and Fe nanoparticle catalysts for the reduction of nitroarenes. These catalysts showed relatively high selectivity toward aromatic amines, but the activity was much lower than that of gold.[12−14] It is very important that an efficient, cost-effective, and chemoselective catalyst be developed for the hydrogenation of nitroarenes.

Atomic layer deposition (ALD) is a layer-by-layer gas phase process, which has been employed to uniformly deposit conformal films on porous nanostructures.[20,21] The growth of these films can be controlled at the atomic level through self-limiting, sequential binary reactions on the substrate surface. ALD also allows the uniform deposition of highly dispersed metal nanoparticles (2 nm or smaller). Metal nanoparticles, such as Pt and Pd, have been successfully deposited on a porous substrate by ALD.[22,23] This is very important for the metal nanoparticles in catalysis application, especially for supported catalysts.[22] These advantages have expanded the ALD applications in the catalysis area. As a part of our effort in this area, we demonstrated the excellent performance of platinum nanoparticles deposited by ALD for different liquid phase catalytic reactions.[24,25] Recently, Gould et al.[26] demonstrated that Ni nanoparticles deposited by ALD had excellent performance in propylene hydrogenolysis reactions. It was demonstrated that smaller metal nanoparticles showed higher activity for hydrogenation of nitroarenes.[11,27] It is expected that nickel nanoparticles deposited by ALD would have excellent properties for the reduction of NO_2 groups.

Here, we report the chemoselective reduction of aromatic nitro compounds to the corresponding anilines by highly dispersed ALD nickel nanoparticles, supported on SiO_2 in combination with a convenient hydrogen donor. The reaction conditions were optimized using different amounts of hydrazine hydrate. Reduction reactions of different nitroarenes were studied to evaluate the performance of the catalysts.

2. EXPERIMENTAL SECTION

2.1. Materials. All solvents, hydrazine hydrate, and reactants were provided by J&K Chemical. Silica nanoparticles (20−30 nm in diameter) and silica gel particles were purchased from US Research Nanomaterials and Sigma-Aldrich, respectively. The silica gel particles were 30−75 μm in diameter with an average pore size of 15 nm and a Brunauer−Emmett−Teller surface area of ~270 m^2/g. Bis(cyclopentadienyl)nickel was purchased from Alfa Aesar.

2.2. Ni Nanoparticles Deposited on SiO_2 by ALD. Ni ALD was carried out using bis(cyclopentadienyl)nickel

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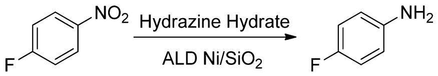
Table 1. Evaluation of the Effects of Hydrazine Amounts and Solvent on the Reduction of 4-Fluoronitrobenzene to *p*-Fluoroaniline Catalyzed by One Cycle of Ni ALD-Deposited on Silica Gel Particles[a]



Entry	Catalyst	Temp (°C)	Solvent	NH_2NH_2, equiv	Selectivity (%)	Yield (%)
1	no catalyst	100	EtOH	4	0	0
2	Ni/SiO_2	60	EtOH	4	98.1	59.2
3	Ni/SiO_2	80	EtOH	4	97.8	75.8
4	Ni/SiO_2	100	EtOH	4	98.2	95.0
5	Ni/SiO_2	120	EtOH	4	97.9	71.7
6	Ni/SiO_2	100	EtOH	6	98.1	96.5
7	Ni/SiO_2	100	EtOH	8	98.2	97.8
8	Ni/SiO_2	100	THF	8	97.5	92.7
9	Ni/SiO_2	100	CH_3OH	8	97.9	94.2
10	Ni/SiO_2	100	*t*-BuOH	8	98.5	95.8
11	recycle1	100	EtOH	8	98.5	95.7
12	recycle2	100	EtOH	8	98.0	95.2
13	recycle3	100	EtOH	8	97.8	94.3
14	recycle4	100	EtOH	8	97.2	94.0

[a] Reaction conditions: 6 mmol of nitroarenes, 4−8 equiv of NH_2NH_2, 10 mL of solvent, and 10 mg of Ni/SiO_2 catalysts (except entry 1) were added into the reactor. The reactions were carried out at different temperatures for 8 h.

($NiCp_2$) and hydrogen as precursors at 300 °C in a fluidized bed reactor. The ALD reactor system was described in detail previously.[28] Both silica nanoparticles (20−30 nm) and porous silica gel particles were used as substrates. In this study, one cycle of Ni ALD was applied on the silica gel particles, and different cycles of Ni ALD were applied on the silica nanoparticles. The details of Ni ALD are introduced in the Supporting Information.

2.3. General Procedure of Nitroarenes Reduction with Hydrazine Hydrate Catalyzed by Ni/SiO_2. Hydrazine hydrate was chosen as the hydrogen donor for the reduction of aromatic nitro compounds. Ni supported on silica gel particles was applied to catalyze the reaction. In a typical reaction, nitroarenes (6 mmol), NH_2NH_2 (4−8 equiv), solvent (10 mL), and Ni/SiO_2 catalysts (10 mg) were added into a sealed copper tube with an open end and 12 mL in volume. The reaction was carried out at atmospheric pressure and an appropriate temperature (see Table 1). The products of the reaction were monitored by a LC-20AT high-performance liquid chromatography equipped with a Hypersil ODS (C18) column and SPD-20A/20AV UV−vis detector. Methanol and water (80% methanol and 20% water) were employed as the mobile phase at a flow rate of 1 mL/min. The mixture was separated at 25 °C with 254 nm as the detection wavelength. The identities of all products were compared with authentic samples. For the recycling studies of 4-fluoronitrobenzene reduction with hydrazine hydrate, the reaction conditions were as follows: 6 mmol of 4-fluoronitrobenzene, 10 mg of Ni/SiO_2, 48 mmol of hydrazine hydrate (in each cycle), and 10 mL of ethanol, for 8 h at 100 °C. After each run, the catalyst (Ni/SiO_2) was isolated by a magnet and rinsed thoroughly with ethanol, since the Ni/SiO_2 particles were highly magnetic.

2.4. Catalyst Characterization. Inductively coupled plasma-atomic emission spectroscopy (ICP−AES) was employed to analyze the Ni content of the catalysts. The Ni particles were directly observed by high-resolution transmission electron microscopy (HRTEM). X-ray photoelectron spectroscopy (XPS) was applied to verify the composition of Ni on the silica particles. Fourier transform infrared spectroscopy (FTIR) was employed to verify the complete removal of the organic ligand from the ALD precursor.

3. RESULTS AND DISCUSSION

3.1. Characterization of Ni/SiO_2. The ICP−AES result showed that the Ni loading of one cycle of Ni ALD on the silica gel particles was 0.73 wt %. Figure 1 shows the HRTEM images of ALD-deposited Ni nanoparticles (2 cycles and 15 cycles) on 20−30 nm silica nanoparticles and the size distribution of the Ni nanoparticles. The average size of the Ni nanoparticles was 2.4 and 2.6 nm for the 2 cycle- and 15 cycle-samples, respectively. This particle size was similar to the values reported by Gould et al.[26] We believe that the average size of Ni nanoparticles deposited on silica gel particles, with only 1 cycle of Ni ALD, should be ∼2.4 nm or even smaller. The TEM images also indicated that the Ni nanoparticles were highly dispersed on the silica support. Figure S1 shows the Ni (2p) high-resolution XPS spectrum for Ni supported on a silica gel sample. Carbon peaks were also observed on the survey scan of the XPS spectrum (Figure S2). To verify whether there were substantial organic ligands from the Ni precursor left on Ni particles, FTIR was applied to analyze the organic groups. Figure S3 shows that there were no characteristic peaks for the cyclopentadienyl group. This means that all organic groups of the precursor were removed during the ALD hydrogen reduction process.

3.2. Catalytic Reduction of 4-Fluoronitrobenzene. To optimize the reaction conditions, the reduction of 4-fluoronitrobenzene was initially investigated with different amounts of hydrazine and different solvents at different temperatures (Table 1). Ni/silica gel particles were used as catalysts in all catalytic reactions. The recyclability of the catalyst was also investigated by recycling the catalyst for reduction of 4-fluoronitrobenzene. As shown in Table 1, the control experiment showed that no reaction was processed without a catalyst. The temperature was a key factor in the reduction of 4-fluoronitrobenzene. At 60 °C, when 4 equiv of hydrazine hydrate was added, the selectivity to *p*-fluoroaniline was 98.1%, and the yield was only 59.2%. The yield increased

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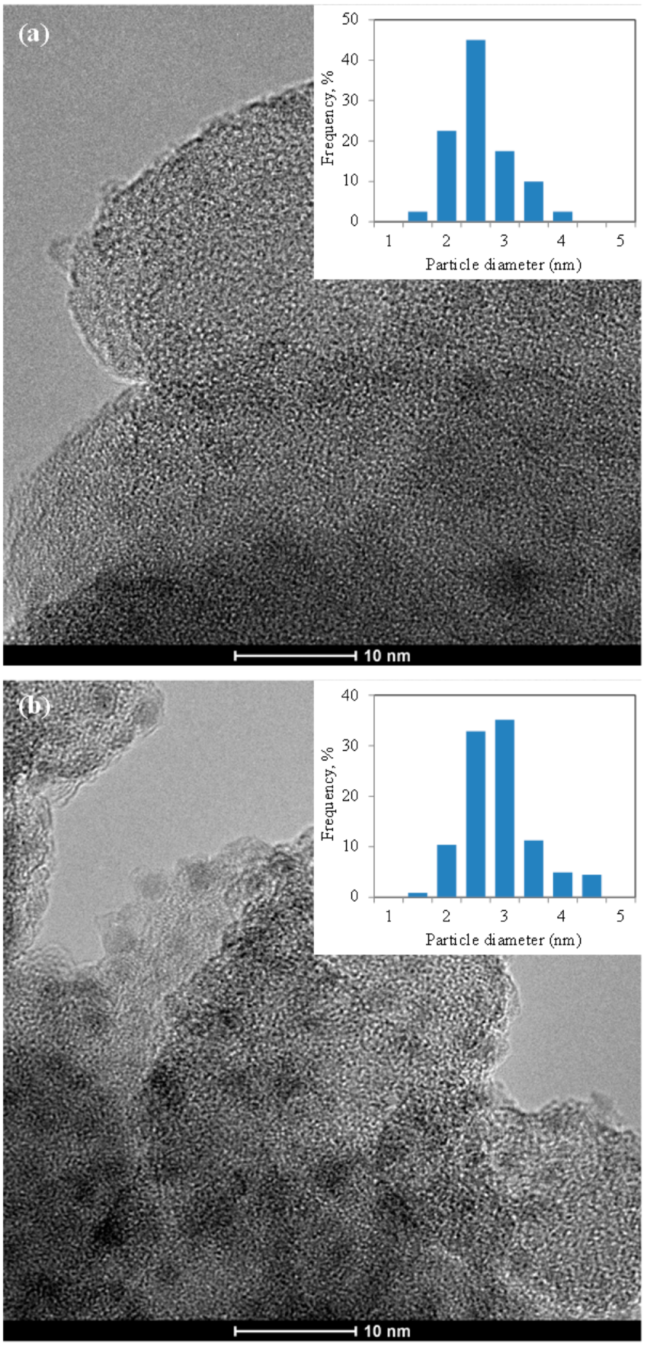


Figure 1. HRTEM images of (a) 2 cycles and (b) 15 cycles of ALD-deposited Ni nanoparticles on 20−30 nm silica particles. The inlet images show the size distribution of Ni nanoparticles.

with increases in the temperature up to 100 °C (75.8% at 80 °C and 95.0% at 100 °C); however, both selectivity and yield decreased at 120 °C, which was due to some side reactions at higher temperatures. On the basis of this initial study, 100 °C was selected as the reaction temperature in the following studies. At 100 °C, the yield increased to 96.5% and 97.8% when the hydrazine amount was increased to 6 and 8 equiv, respectively. Solvents normally have a significant influence on the performance of the catalyst.[29,30] In this study, the different solvents (tetrahydrofuran (THF), methanol, and tertiary butanol) were used for this reaction. The selectivity and yield showed no significant differences, which indicated that the solvents would not affect this reaction in this catalytic system. The ALD-prepared Ni/SiO_2 catalysts were highly magnetic; therefore, for separation, the catalyst particles could be easily collected using a magnet. The catalyst particles were recycled four times. Both the selectivity and yield only slightly decreased after cycling, as shown in Table 1, which indicated that the ALD-prepared Ni/SiO_2 catalysts could maintain good activity and stability in the liquid phase reactions.

3.3. Reduction of Nitro Compounds into Amines with Hydrazine Hydrate Catalyzed by Ni/SiO_2. To investigate and determine the scope and limitations of this reductive methodology, a series of nitroarenes were examined. As shown in Table 2, for a reaction time of 8 h, the selectivity and yield of most nitroarene reduction reactions were higher than 90%. For example, the selectivity and yield of aniline were 95.2% and 93.8%, respectively. Turnover frequency (TOF), which is defined as the reactant molecules reacting per active site in unit time, was calculated to investigate and determine the activity of the catalyst (Table 2). The conversion of nitroarenes was close to 100% for 8 h of reaction; thus, it would not be accurate to calculate TOF at that high conversion. To calculate an accurate TOF, reactions were also carried out for 2 h. The active metal surface area (ASA) and dispersion of the catalysts were calculated by using the measured size of the Ni nanoparticles in eqs 1 and 2:[26]

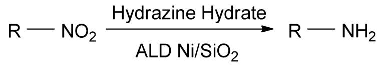
$$\mathrm{ASA}\ (\mathrm{m}^2/\mathrm{g}) = \frac{L \times f}{d \times z} \tag{1}$$

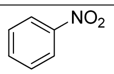
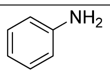
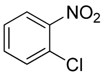
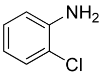
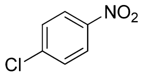
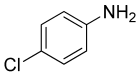
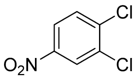
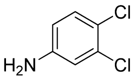
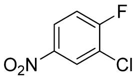
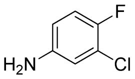
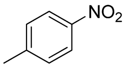
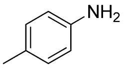
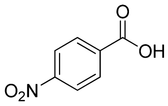
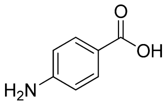
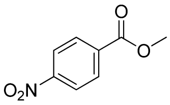
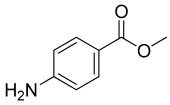
$$\mathrm{dispersion}\ (\%) = \frac{\mathrm{ASA} \times M}{N \times A \times L} \tag{2}$$

where L is the weight fraction of metal loading, f is the particle shape correction factor ($f = 6$ for a sphere), d is the average diameter of the supported particles measured by TEM (assume the size of Ni particles on silica gel is 2.4 nm), z is the metal density, M is the formula weight of the supported metal, N is Avogadro's number, and A is the metal atomic surface area (for Ni, $A = 6.494$ Å^2/atom). On the basis of eq 1, the ASA for the Ni/SiO_2 catalyst is 2.05 m^2/g. The metal dispersion was then calculated from eq 2 to be 42%. On the basis of the conversion and reaction time (conversion at a reaction time of 2 h), the TOF was calculated. As shown in Table 2, almost all of the TOF of entries 1−8 were higher than 0.7 s^{-1}, which is pretty high in the reduction of nitroarene systems.

Liu et al.[9] applied Au/meso-CeO_2 as the catalyst for the reduction of nitrobenzene and got a TOF of 20 h^{-1} (5.56×10^{-3} s^{-1}). Petkar et al.[13] employed a Fe−Ni bimetallic system to catalyze the reduction of aromatic nitro compounds and got a TOF of 4.76×10^{-3} s^{-1} for nitrobenzene. As shown in Table 2, the TOF of nitrobenzene in our system was 0.78 s^{-1}, which was more than 2 orders of magnitude higher than the reported values. The high catalytic activity of the catalysts could be due to the highly dispersed Ni nanoparticles prepared by ALD. In the above-mentioned previous studies, the metal nanoparticle catalysts were normally prepared by the liquid impregnation method, and the metal nanoparticles were very large. In our current study, the Ni nanoparticles were prepared by ALD, and the particle sizes were smaller than 3 nm. The effect of particle size on the catalytic activity was reported previously. Mahata et al.[27] reported that smaller Ni nanoparticles showed higher activity for hydrogenation of nitroarenes. Shimizu et al.[11] also demonstrated that catalyst activity increased with the decrease in silver nanoparticle size for hydrogenation of nitroarenes. In addition, Gould et al. reported that the surface structures of the

Table 2. Chemoselective Reduction of Nitro Compounds to Amines with Hydrazine Hydrate Catalyzed by 1 Cycle of Ni ALD-Deposited on Silica Gel Particles



Entry	Reactant	Product	Selectivity (%)[a]	Yield (%)[b]	TOF (s^{-1})[c]
1			95.2 (95.8)	93.8 (45.4)	0.78
2			94.2 (94.5)	92.7 (42.7)	0.75
3			94.0 (95.0)	91.9 (41.5)	0.72
4			95.7 (95.5)	93.7 (42.6)	0.74
5			96.0 (96.3)	94.7 (43.3)	0.74
6			94.8 (94.9)	92.1 (41.1)	0.72
7			87.1 (89.3)	74.8 (37.4)	0.69
8			89.2 (90.5)	76.1 (38.7)	0.71

Reaction conditions: 6 mmol of nitroarenes, 48 mmol of NH_2NH_2, 10 mL of ethanol, and 10 mg of Ni/SiO_2 catalysts were added into the reactor. The reactions were carried out at 100 °C for 2 and 8 h, respectively. [a]Values in parentheses are the selectivity of the reactions after 2 h. [b]Values in parentheses are the yields of the reactions after 2 h. [c]TOF values were calculated using the results with a reaction time of 2 h.

ALD Ni nanoparticles were different from those of the larger Ni particles prepared by an incipient wetness method.[26] This could also be a reason for the high catalytic activity of the catalysts.

The hydrogenation of nitroarenes often stops at an intermediate stage, yielding various byproducts. For hydrogenation of halogenated nitroarenes, the hydrogenolysis of the C−X, in which X represents halogen, always happens.[31] Because of the high activity of ALD Ni nanoparticles, the hydrogenation of nitroarenes did not stop at the intermediate stage. The Ni nanoparticles also showed no activity in hydrogenolysis of the C−X bond in our current study, since no dehalogenation products were observed. Gawande et al.[32] also reported that no dehalogenation occurred in the hydrogenation of halogenated nitroarenes using Fe_3O_4−Ni nanoparticles. This was our hypothesis for the high selectivity of our ALD Ni catalysts. More studies are being conducted to reveal the effects of the Ni particle size on the activity and selectivity of the reactions.

The ALD catalysts showed excellent selectivity and yield of the reduction of nitroarenes with fluorine and chlorine. In particular, no defluorination and dechlorination byproducts were observed (entries 2−5), and the selectivities of all reactions were higher than 94%. This result was very good compared with other reported results with different kinds of catalyst systems in which the selectivities were always lower than 90% or even lower.[9,30,33] The high selectivity of the reaction is highly desirable in industry because these byproducts do not need to be separated, which is a costly process. For example, for entry 5, the product is solely 3-chloro-4-fluoro-benzenamine, which is a raw material for norfloxacin. The effective control of defluorination and dechlorination could help provide high-purity raw material for norfloxacin; however, the selectivity and yield of the transfer hydrogenations of *p*-nitrobenzoic acid and methyl *p*-nitrobenzoate were lower than 90% and 80%, respectively. This was possible largely because of the existence of other electron-withdrawing groups on the reactant molecules. Compared with the reported catalytic systems, our catalytic system is much simpler in terms of both catalyst preparation and experimental procedure. It is an efficient, cost-effective, and chemoselective catalyst for the reduction of nitroarenes.

4. CONCLUSIONS

Highly dispersed nickel nanoparticles were deposited on both porous silica gel particles and 20−30 nm dense silica nanoparticles. The prepared Ni/silica gel catalysts can activate hydrazine hydrate as a reducing agent in the transfer hydrogenation of aryl nitro compounds into the corresponding amines with high selectivity and high yield. To the best of our knowledge, this is the first report of ALD-prepared nickel nanoparticles for the transfer hydrogenation of aryl nitro compounds. The current work has extended the utility of a readily available catalyst (Ni/SiO_2) toward new applications in catalysis and organic chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00969.

Ni ALD experimental details, characterization details of XPS and FTIR, XPS spectra, and FTIR spectra (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: liangxin@mst.edu.

Author Contributions

§C.J. and Z.S. contributed equally.

Notes

The authors declare no competing financial interest.

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