Highly active layered double hydroxide-derived cobalt nano-catalysts for p-nitrophenol reduction

Hanyu Ma [a,1], Haitao Wang [a,1], Tong Wu [a], Chongzheng Na [a,b,*]

[a] Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, IN 46556, USA
[b] Department of Civil, Environmental, and Construction Engineering, Texas Tech University, Lubbock, TX 79409, USA

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ABSTRACT

Replacing precious noble-metal catalysts with non-precious metal ones is a well-recognized strategy for reducing the cost of catalytic water treatment. The implementation of this strategy is, however, challenging. To reduce the cost by using non-precious metal catalysts, the reactivity ratio between non-precious and precious metal catalysts must exceed their price ratio. Here, we report for the first time that the parity condition has been surpassed for cobalt (Co), in comparison to the most active precious metal catalyst made of palladium, in the catalytic reduction of p-nitrophenol with borohydride. This is achieved by affixing Co nanoparticles on two-dimensional layered double oxide (LDO) nano disks through thermal phase transformation of cobalt-magnesium–aluminum layered double hydroxide precursors. We show that the catalytic activity of LDO–Co is a function of Co molar fraction among metal cations. The highest reactivity is achieved at a molar fraction of 28%, giving a pseudo first order rate constant of $86(\pm 3)\,min^{-1}$ at $25\,°C$ for a catalyst dose of $1\,g\,L^{-1}$ (as Co) and an initial p-nitrophenol concentration of 0.2 mM. Compared to other Co nano-catalysts described in the literature, the LDO–Co design has improved the reactivity of cobalt by at least 49 times. We further show that the high reactivity of LDO–Co remains after repeated reuse as well as after borohydride is replaced by formate, a moderate reductant and hydrogen donor. We propose that the high reactivity and superior longevity of LDO–Co are results of the heteroepitaxial fixation of cobalt on LDO through cobalt–oxygen bonds that are similar to those in spinel cobalt oxide.

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1. Introduction

An important challenge for developing catalysts for water treatment and environmental remediation is to reduce the cost associated with catalyst fabrication and restocking. One potential solution is replacing the commonly used but expensive 4d and 5d precious noble metal catalysts such as palladium (Pd) and platinum (Pt) with inexpensive 3d non-precious metal catalysts such as cobalt (Co) and nickel (Ni). Because non-precious metal catalysts are usually much less reactive than those made of precious metals, a financial gain can only be made when the ratio of their reactivities exceeds the ratio of their prices. Reaching this cost parity is, however, challenging in spite of recent advances in the design and synthesis of nano-sized catalysts. According to the London Metal Exchange, cobalt and palladium have a price ratio of approximately

1:750. According to their reactivities in catalyzing the model reaction of p-nitrophenol reduction by borohydride, the ratio of their mass-normalized reactivities is less than 1:1000 [1,2], suggesting a discouraging economic loss if cobalt is used to replace palladium to remediate p-nitrophenol.

The mass-normalized reactivity of nano-catalysts is directly correlated to their stability against aggregation [3]. To prevent aggregation, palladium nanoparticles have been prepared using a variety of stabilizing agents, including dendrimers [2], peptides [4], alumina (Al_2O_3) particles [5], and carbon nanotubes [6]. For the catalyzed reduction of p-nitrophenol by borohydride, the mass-normalized rate constants of palladium catalysts range over nearly 4 orders of magnitude from $k = 1.0$ to $6.9 \times 10^3\,min^{-1}\,g^{-1}\,L$, with the most active palladium nanoparticles created under the stabilization of dendrimers [2,7]. In comparison, only limited efforts have been given to finding the appropriate stabilizers for nanoparticles made of non-precious metals such as cobalt. Examples of stabilizers for cobalt nanoparticles include reduced graphene oxide [8,9], hydrogel [10], and silica (SiO_2) cage [11], yielding $k = 0.82$–$30.8\,min^{-1}\,g^{-1}\,L$ in the catalyzed reduction of p-nitrophenol by borohydride. Compared to unsupported cobalt

nanoparticles [12], only 2 orders of magnitude of improvement have been achieved using these stabilizing supports, much lower than the improvement made by stabilizing agents for palladium nano-catalysts.

Well-dispersed cobalt nanoparticles can be made by the topotactic transformation of layered double hydroxide (LDH) nanodisks [13]. LDH is a group of pseudo two-dimensional crystals having a structure similar to hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}\cdot4(H_2O)$) [14]. This structure consists of alternating layers of metal oxides and intercalated water and anions. The disks often have a nominal diameter of micrometers but a thickness of only tens of nanometers. Cobalt has an ionic radius similar to that of magnesium; therefore, Co-containing LDH can be readily prepared by replacing part of magnesium with cobalt [15]. LDH is then calcined in the presence of hydrogen (H_2) gas above 600 °C, which separates Co from LDH and reduces it to the metallic nanoparticles [16]. The calcination also transforms LDH to layered double oxide (LDO) with a spinel ($MgAl_2O_4$) structure by removing intercalated water and carbonate anions [17]. Although spinel does not have a layered structure, because the platy morphology of LDH is largely preserved during calcination, the LDH derivative is often referred to as layered double oxide or LDO [18,19]. LDO-supported Co nanoparticles (LDO–Co) have been shown to be active in catalyzing hydrogenation reactions [20–23], steam reforming [24–30], aldol condensation [31], thermal decomposition [32,33], oxidation and combustion[34,35], and carbon nanotube synthesis [36–39].

LDH and the calcined derivative LDO have been previously investigated for water treatment and environmental remediation, utilizing their abilities of contaminant adsorption [40]. Here, we report the application of LDH-derived cobalt nano-catalysts for catalyzing the degradation of model contaminant p-nitrophenol. p-Nitrophenol is a Clean Water Act priority pollutant, which has an acceptable daily intake (ADI) of 0.32 mg per day over a month [41]. The toxicity of p-nitrophenol can be lowered significantly after it is reduced to p-aminophenol, which has a negligible ADI of 4.55 mg per day over lifetime [42]. We show that LDO–Co surpasses all the cobalt-based catalysts reported so far in the literature in catalyzing the reduction of p-nitrophenol by borohydride, giving a relative reactivity ratio of LDO–Co with the most active dendrimer-stabilized Pd nano-catalysts exceeding the price ratio of cobalt and palladium. Our results indicate that economic incentives exist for replacing palladium with cobalt in similar applications. Furthermore, we show that the high reactivity of LDO–Co retains with repeated use and is transferable when a more realistic hydrogen donor such as formate is used in place of borohydride. We propose that the reactivity and longevity of LDO-supported cobalt nanoparticles can be attributed to the superior stability resulting from heteroepitaxial fixation through interfacial Co-O bonds similar to those in spinel cobalt oxide.

2. Experimental section

Reagent-grade chemicals were purchased from Sigma–Aldrich except otherwise specified. Deionized (DI) water was generated on site using a Millipore system.

2.1. Preparation and characterization of LDO–Co

Urea ($CO(NH_2)_2$), aluminum nitrate ($Al(NO_3)_3$), magnesium nitrate ($Mg(NO_3)_2$), and cobalt nitrate ($Co(NO_3)_2$) were dissolved in 100 mL DI water, resulting in a urea concentration of 100 mM and a total metal concentration of 50 mM. The molar ratio of divalent magnesium and cobalt to trivalent aluminum was kept constant at 2:1. The molar percentage of cobalt with regard to all metals, θ, was varied from 0 to 67% (note: no Mg at $\theta=67\%$).

LDH was synthesized in a sealed autoclave reactor at 100 °C in 12 h. LDH powder was collected by centrifugation, washed with DI water, and freeze–dried (Labconco Freezone 4.5). The powder was then placed inside a sealed quartz tubing and heated in a tube furnace to 600 °C under argon protection. Hydrogen was introduced into the quartz tubing at 50 sccm for 20 min to carry out thermal phase transformation. LDH, LDO, and LDO–Co were characterized using transmission electron microscopy (TEM; FEI Titan 300–80), scanning electron microscopy (SEM; FEI Magellan 400), atomic force microscopy (AFM; Park Systems XE 70), and powder X-ray diffraction (XRD; Bruker D8 Advance Davinci). Sample preparation and analyses were made following standard procedures. Metal contents in LDO–Co were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES; PerkinElmer Optima 2000DV) after LDO–Co was completely digested in 70% nitric acid.

2.2. Catalytic reduction of p-nitrophenol by borohydride

A working suspension of LDO–Co was prepared by dispersing 2 mg LDO–Co in 8 mL DI water. The suspension was sonicated for 10 min to ensure complete dispersion. 0.75 mL working suspension was mixed with 32 mM $NaBH_4$ at a 1:1 volumetric ratio and shaken for 2 h to reduce any oxidized cobalt nanoparticles back to metallic cobalt. The mixture was then transferred into a standard UV/vis quartz cuvette. Another 1.5 mL $NaBH_4$ (32 mM) and 30 μL p-nitrophenol (20 mM) were added to the cuvette to initiate the p-nitrophenol reduction. The reaction solution was stirred with a small magnetic bar. The light absorption from 220 to 520 nm by the reactive solution was recorded every 30 s with a UV/vis spectrophotometer (Agilent Cary 300). A baseline absorbance was established using a 3-mL mixture consisting of LDO-Co and $NaBH_4$ but not p-nitrophenol. After subtracting the baseline, absorbance was converted to concentration using a calibration curve obtained with p-nitrophenol solutions of known concentrations.

2.3. Co nanoparticles loosely attached to LDO (LDO–Co*)

LDO–Co* was prepared in two steps. First, 20 mg LDO ($\theta=0$) and 46.5 mg $Co(NO_3)_2\cdot9H_2O$ were added to 10 mL DI water under 10-min sonication and mixed on a shaking table for 24 h. LDO nanodisks with adsorbed Co^{2+} were then collected by centrifugation, washed with DI water for three times, and freeze–dried. Second, 12.5 mg LDO adsorbed with Co^{2+} was dispersed in 10 mL 32 mM $NaBH_4$ solution to reduce Co^{2+} to metallic Co. After 2 h, LDO–Co* was collected by centrifugation and used to catalyze the reduction of p-nitrophenol by borohydride. To do so, 1.5 mL suspension containing 1.25 g L^{-1} LDO–Co* was mixed with 1.5 mL $NaBH_4$ (32 mM) and 30 μL PNP (20 mM) in a quartz cuvette.

2.4. Catalytic reduction of p-nitrophenol by formate

The reaction was conducted in a 50-mL 3-neck flask immersed in water, which isolated contents inside the flask from air. 5 mg LDO–Co with $\theta=28(\pm2)\%$ was dispersed in 18.5 mL DI water by sonication and transferred into the flask. The solution was purged by N_2 at a flow rate of 60 sccm and mixed by a magnetic stir bar. The gas was released from the flask into air through a thin tubing. After 2 h, 1 mL DI water containing 10 mg $NaBH_4$ was added to reduce oxidized cobalt into metallic cobalt. After another 2 h, a mixture of 0.5 mL sodium formate (HCOONa, 2.0 M) and p-nitrophenol (8.0 mM) was injected into the flask to start the reaction. A control experiment was performed following the same protocol without adding sodium formate.