Mild and Selective Hydrogenation of Nitrate to Ammonia in the Absence of Noble Metals

Lin Wei
*Iowa State University, lwei@iastate.edu*

Da-Jiang Liu
*Ames Laboratory, dajiang@ameslab.gov*

Bryan A. Rosales
*Iowa State University*

James W. Evans
*Iowa State University and Ames Laboratory, jevans@ameslab.gov*

Javier Vela
*Iowa State University and Ames Laboratory, vela@iastate.edu*

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Keywords
Nitrate removal, nitrate reduction, catalytic hydrogenation, Ni2P catalysts, non-precious metal, noble metalfree, high selectivity, ammonia

Disciplines
Chemistry | Environmental Chemistry

Comments
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Mild and Selective Hydrogenation of Nitrate to Ammonia in the Absence of Noble Metals

Lin Wei,1 Da-Jiang Liu,2 Bryan A. Rosales,1 James W. Evans,2,3 Javier Vela*1,2

1Department of Chemistry, Iowa State University, 2Ames Laboratory, 3Department of Physics & Astronomy, Iowa State University, Ames, Iowa 50011, USA

KEYWORDS. Nitrate removal, nitrate reduction, catalytic hydrogenation, Ni2P catalysts, non-precious metal, noble metal-free, high selectivity, ammonia.

ABSTRACT: Motivated by increased awareness about nitrate contamination of surface waters and its deleterious effects in human and animal health, we sought an alternative, non-noble metal catalyst for the chemical degradation of nitrate. First-row transition metal phosphides recently emerged as excellent alternatives for hydrogen evolution and hydrotreating reactions. We demonstrate that a key member of this family, Ni2P readily hydrogenates nitrate (NO3−) to ammonia (NH3) near ambient conditions with very high selectivity (96%). One of the few non-precious metal-based catalysts for this transformation, and among ca. 1% of catalysts with NH3 selectivity, Ni2P can be recycled multiple times with limited loss of activity. Both nitrite (NO2−) and nitric oxide (NO) intermediates are also hydrogenated. Density functional theory (DFT) indicates that—in the absence of a catalyst—nitrite hydrogenation is the reaction bottleneck. A variety of adsorbates (H, O, N, NO) induce surface reconstruction with top-layer Ni-rich surface stoichiometry. Critically, H saturation coverage on Ni2P(001) is only ca. 3 nm−2, significantly less than that on Pd(111) and Ni(111) of ca. 15–18 nm−2, which may play a key role in allowing coadsorption of NO3−. The ability of Earth-abundant, binary metal phosphides such as Ni2P to catalyze nitrate hydrogenation could transform and help us better understand the basic science behind catalytic hydrogenation and, in turn, advance the next generation of oxyanion removal technologies.

INTRODUCTION

Access to clean water is an essential prerequisite for communities to prosper.1 Unfortunately, higher demand for agricultural products incentivizes the use of ever more land for crop production, limiting the amount of low-lying prairie, riparian forests, and wetlands available for fertilizer biodegradation. Normally, these areas contain minimum oxygen zones that remove some of the toxic contents of agricultural runoff, for example through the anammox biodentification process.2,3 Without these, streams, rivers, and groundwater can end up with high concentrations of nitrate—among phosphate and other—ions, which is responsible for birth defects—infant methemoglobinemia or ‘blue baby’ syndrome6,7—and thyroid8,9,10 and bladder11,12,13 cancers.14,15 Downstream, this runoff and urban sewage combine to deliver vast amounts of nitrogen and phosphorus to the sea. In the Gulf of Mexico, this creates one of the largest recurring hypoxic zones in the world—8,776 square miles in 2017—larger than the State of Massachusetts. For these reasons, millions of dollars are spent each year on water purification, and millions more are lost from missed commercial and recreational opportunities.16

Removing nitrate (NO3−) from water is a difficult task. Under normal, aerobic conditions, NO3− is a weakly coordinating, thermodynamically stable, and kinetically persistent form of nitrogen. The water utility of a midsize (pop. 0.5 M) American city in a heavily agricultural region spends ca. $1–2 million USD annually to physically remove nitrate.17 Critically, available physical separation methods—reverse osmosis, ion exchange, and electrodialysis—leave nitrate ions intact, and significant amounts of these are reintroduced into the environment after the process is complete. An alternative chemical degradation method for nitrate removal is hydrogenation.16,19 Nitrate hydrogenation is a spontaneous energy releasing process (ΔG < 0) by which hydrogen gas (H2) is used to reduce nitrate to a potentially more useful or benign form of nitrogen, such as ammonia (NH3) or dinitrogen (N2), respectively (Scheme 1 and Table 1).

Scheme 1. (a) Catalytic NO3− hydrogenation and (b) some of its common intermediates.

Table 1. Selected nitrate (NO3−) hydrogenation reactions under acidic conditions.
Unfortunately, nitrate hydrogenation technologies are presently limited by a lack of basic knowledge. Multiple “bimetallic” catalysts for this transformation exist; each consists of a mixture of two metal particles, at least one of which is made of a scarce and expensive noble metal—Ru, Pd, or Pt—which decreases their potential utility and prevents their large-scale deployment. A few reports with base metals exist. Compounding this problem, some nitrate reduction methods suffer from limited activity and/or poor yields. Many they tend to be unselective, often producing nitrite (NO₂⁻) or other partially reduced byproducts (NO, NO₂) that are as toxic or more so than nitrate itself (Scheme 1a).

In recent years, binary phosphides (M₂P) of the late first row transition metals (M = Mn, Fe, Co, Ni, Cu) emerged as excellent alternatives to noble metal catalysts for the hydrogen evolution reaction (HER). Chief among these is dinickel phosphide (Ni₂P), whose reconstructed surface structure may mimic the active site of [NiFe] hydrogenase. Initially thought to be a semiconductor, electronic structure calculations revealed that bulk Ni₂P is actually metallic. Interestingly, their resemblance to noble metals goes well beyond HER, as first row transition metal phosphides are also active catalysts in hydrotreating (HDX, X = S or hydrodesulfurization, O or hydrodeoxygenation, and hydrodenitrogenation), alkane hydrogenation, and hydrodearomatization reactions. The ability of Ni₂P and other Earth-abundant, binary metal phosphides to readily and reversibly adsorb hydrogen (H₂) perform a wide range of hydrogenation-like reactions, and achieve high product selectivities strongly suggest that they could also catalyze the hydrogenation of other, typically more challenging reactants, such as nitrate (NO₃⁻).

In this paper, we demonstrate that Ni₂P is capable of quickly and completely hydrogenating NO₃⁻ under near ambient conditions. The reaction is highly selective toward ammonia (NH₃), a potentially reusable form of nitrogen, which becomes protonated under the reaction conditions to ammonium (NH₄⁺). Control experiments confirm this is one of the very first low pressure, NO₃⁻ hydrogenation catalysts based on a non-precious, base metal, whereas the high selectivity for NH₄⁺ is distinctive from that of many other conventional noble-metal containing, bimetallic systems.

### RESULTS AND DISCUSSION

**General observations.** Based on our previous work on the phase-selective synthesis of binary nickel phosphides, we prepared Ni₂P nanocrystals from the reaction of nickel(II) acetate with triphenylphosphine in oleylamine and 1-octadecene at 275 °C (Figure 1). Many other earlier and later Ni₂P preparations are available. Without further modification, as made Ni₂P nanocrystals have little catalytic activity. However, annealing under H₂ at 400 °C for 1 h greatly enhances the activity of Ni₂P nanocrystals toward NO₃⁻ hydrogenation (Figure 2). Structural characterization shows that the bulk of the nanocrystals remains unchanged after H₂ annealing (Figure 1—see Supporting Information or S.I.). Peak widths in the powder X-ray diffraction (XRD) patterns before and after H₂ annealing correspond to a similar Scherrer size of 18 nm (Figure 1). This agrees well with prior studies geared toward catalytic HER and HDX reactions, which showed that the main effect of H₂ annealing on Ni₂P nanocrystals is to remove ligands from their surface (see also removal of adventitious surface species below).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔG°</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₃⁻ + H₂ + H⁺ → HNO₂ + H₂O</td>
<td>-158 kJ/mol</td>
</tr>
<tr>
<td>2NO₃⁻ + 5H₂ + 2H⁺ → N₂ + 6H₂O</td>
<td>-1118 kJ/mol</td>
</tr>
<tr>
<td>NO₃⁻ + 4H₂ + 2H⁺ → NH₄⁺ + 3H₂O</td>
<td>-611 kJ/mol</td>
</tr>
</tbody>
</table>

*ΔG° Gibbs free energy change at pH 2.*
Activated Ni$_2$P catalyzes the ambient (1 atm H$_2$) hydrogenation of aqueous NO$_3^-$ at 60 °C (“H$_2$-anld Ni$_2$P” in Figure 2). When the reaction is started at a relatively low pH such as 2 or 4, it is accompanied by a progressive increase in pH (see below). The reaction is faster under relatively acidic compared to neutral conditions (Figure 3). At pH 2—achieved by acidification with either HCl or H$_2$SO$_4$, bubbling of H$_2$ through a 1.6 mM solution of NO$_3^-$ in water reduces its concentration to 0.55 mM (66% conversion) within 1 h, and to 0.02 mM (99% conversion) within 4 h. For comparison, 1.6 mM or 22.5 mg/L NO$_3^-$-N is ca. twice the maximum level of “nitrogen in nitrate” in drinking water as established by the U.S. Environmental Protection Agency (EPA, ≤ 10 mg/L) and the World Health Organization (WHO, ≤ 11.3 mg/L). At pH 4, NO$_3^-$ is completely reduced within 24 h. At neutral pH, a NO$_3^-$ concentration of 1.3 mM remains (19% conversion) after 24. To our knowledge, there are only a few reports of non-noble metal catalysts for NO$_3^-$ hydrogenation. Further, this is one of the first observations of a noble-metal-free hydrogenation catalyst displaying complete (100%) NO$_3^-$ reduction under near ambient conditions.

To gain a deeper insight into the relative activity of Ni$_2$P, we performed identical NO$_3^-$ hydrogenation experiments in parallel, over Ni$_2$P vs. over conventional bimetallic Pd-Cu/SiO$_2$ catalysts. By looking at the low conversion data (≤10-20%, at early reaction times), we estimate that the turnover numbers (TON) and frequencies (TOF) achieved with Pd-Cu/SiO$_2$ are ca. 10-25 times higher than those with Ni$_2$P (see S.I.). However, in terms of reaction rate per gram catalyst (R$_g$), Pd-Cu/SiO$_2$ is comparable or only slightly—0-2 times more active—compared to Ni$_2$P. This implies that Pd-Cu/SiO$_2$ reduces similar amounts of NO$_3^-$ compared to Ni$_2$P when using the same mass of catalysts. Considering the cost and, more importantly, the scarcity of precious metals such as Pd, Ni$_2$P becomes a potentially competitive and perhaps more sustainable substitute to bimetallic catalysts for NO$_3^-$ hydrogenation. In fact, dynamic light scattering (DLS) measurements indicate that the Ni$_2$P catalyst particles may aggregate somewhat following activation by H$_2$-annealing. This agglomeration may hinder some of the Ni$_2$P surface from participating in NO$_3^-$ hydrogenation and may thus reduce catalytic activity. Therefore, we believe that immobilizing the Ni$_2$P nanocrystals on a high surface area SiO$_2$ or another suitable support could help in preventing their aggregation and further increasing their activity and durability.

Figure 3. (a) Effect of pH on NO$_3^-$ hydrogenation activity over Ni$_2$P. (pH values in parenthesis) (b) Consecutive NO$_3^-$ hydrogenation runs over recycled Ni$_2$P at pH 3 (10 mg, 30 mL 1 mM NaNO$_3$, 1 atm H$_2$/Ar, 60 °C, see Experimental).
Unique selectivity for NH₃. Analysis of the aqueous solution after catalysis reveals that the majority (95%) product of NO₃⁻ hydrogenation over Ni₃P is NH₄⁺, with no nitrite (NO₂⁻) being detected. In contrast, conventional bimetallic catalysts (e.g., Pd-Cu/SiO₂) often yield mixtures of products,¹⁹ with NO₂⁻ being the only major product in the absence of the noble metal. Uniquely selective catalysts like Ni₃P, which are capable of producing a single NO₃⁻ hydrogenation product such as N₂ or NH₃ are highly desirable from a practical perspective. When the only product is dinitrogen (N₂), this can simply be released to the atmosphere without causing further harm to the environment. In the rarer—under 1% of catalysts reported to date, see S.I.—but still very valuable case when the only product is ammonia (NH₃ or NH₄⁺), this could potentially be recycled and reused as fertilizer, for example through available NH₄⁺ separation techniques.⁶¹,⁶²,⁶³,⁶⁴,⁶⁵ The economic benefit of the latter is highlighted by the fact that every year, ~17 million tons of ammonia- and urea-based fertilizers are used in the US alone.⁶⁶ A large fraction of these are produced by the energy-intensive Haber–Boßch process which, unlike the system reported here, requires very high temperatures and pressures to operate.⁶⁷

The observed effect of pH on activity suggests a dependence of the reaction kinetics on the concentration of protons.⁶⁸ This can be explained by looking at the overall chemical equation required to hydrogenate nitrate to ammonium, which utilizes two protons to be fully balanced (Table 1). Of these, one H⁺ equivalent is needed for each NO₃⁻ ion that is reduced—the redox reaction per se—while, under the conditions studied here (2 ≤ pH ≤ 7, see above), a second H⁺ equivalent is needed to protonate each NH₃ molecule produced, to its conjugate acid, NH₄⁺ (pK₆ = 9.3).

Catalytic control experiments. To test the true catalytic nature of the Ni₃P nanocrystals, we conducted the following experiments: First, attempts at achieving NO₃⁻ hydrogenation in the absence of Ni₃P were unsuccessful, with null activity or conversion detected after several hours (see S.I.). Second, repeating the reaction with activated Ni₃P but without the flow of H₂ resulted in small but measurable catalytic activity (43% conversion after 12 h). We attribute this residual activity to the presence of hydrogen atoms (H·) adsorbed onto the activated Ni₃P surface, arising from dissociation of H₂ during the annealing step. Once these residual surface-H reactive sites are completely consumed, Ni₃P is no longer active or recyclable unless a continuous flow of H₂ is supplied. In the presence of Ni₃P and H₂ flow, we observe single cycle TON and TOF numbers of up to ca. 24 and 6/h, respectively (see S.I.).

In addition to control experiments, we also tested the recyclability of Ni₃P. Because of the aforementioned increase in pH during hydrogenation, we first sought a way to maintain a relatively low, acidic pH during recycling. However, even relatively inert buffers such as piperazine-N,N’-bis(2-ethanesulfonic acid) (PIPEs) or 2-(N-morpholino)ethanesulfonic acid (MES) failed to maintain the desired pH.⁶⁹ This strongly indicates that, like nitrate, these otherwise noncoordinating alkylsulfonate buffers may be reacting with Ni₃P under our NO₃⁻ hydrogenation conditions. Fortunately, we were able to solve this problem and maintain a pH of ca. 3 throughout our catalytic reactions by continuously adding a concentrated stock solution of acid (see Experimental). In this way, Ni₃P maintains high activity for at least 4 cycles under the flow of H₂, augmenting the overall TON to 45 (Figure 3b & S.I.). A slow decrease in conversion after multiple cycles may be attributed to slow re-passivation of the catalyst surface and/or to partial catalyst etching. Peak widths observed by powder X-ray diffraction (XRD) after 4 catalytic cycles correspond to a Scherrer size of 14 nm, slightly smaller than the 18 nm measured after annealing and before catalysis. Efforts to further improve catalyst stability while maintaining activity, for example by immobilization in a porous support and reannealing under H₂, respectively, are ongoing. Together, these control experiments clearly establish that H₂ flow and substoichiometric amounts of Ni₃P are requisites for sustained NO₃⁻ hydrogenation, affirming that Ni₃P is a catalyst for this reaction.

Probing intermediates. In contrast to NO₃⁻ hydrogenation over the relatively well studied bimetallic catalysts (see above),⁶²,⁷⁰,⁷¹ little is known about the mechanism of NO₃⁻ hydrogenation over Ni₃P. Because nitrite (NO₂⁻) and nitric oxide (NO) are known intermediates in Pd- and Ru-based bimetallic NO₃⁻ hydrogenation, we tested both of these reactants here. Indeed, as is the case for NO₃⁻, aqueous NO₂⁻ is quickly and completely hydrogenated in the presence of Ni₃P under a flow of H₂ (Figure 4a). This is significantly higher than the ~25% NO₂⁻ conversion observed with a zerovalent Ni foam at room temperature.⁷² Compared to NO₃⁻ hydrogenation, NO₂⁻ hydrogenation over Ni₃P is a little faster, even at neutral pH. Interestingly, the reaction selectivity is also different, producing much smaller amounts of NH₄⁺ (Figure 4a). Because no other soluble nitrogen species is detected, we strongly suspected that the remainder nitrogen balance must be gaseous products. To test this hypothesis, we repeated the hydrogenation reaction using ¹⁵N-labeled Na*NO₂ (98%), and easily identified the evolution of singly- and doubly-labeled "¹⁵N₂ (¹⁵N¹⁴N and ¹⁵N²¹N), along with some NO (¹⁵NO) using GC-MS (m/z=29, 30, and 31, respectively) (see S.I.).
Figure 4. (a) Nitrite (NO$_2^-$) hydrogenation over Ni$_2$P (10 mg, 30 mL 1.6 mM NaNO$_2$, initially acidified to pH 2, 1 atm H$_2$/Ar, 60 °C). (b) $^{15}$NO$_2^-$ hydrogenation over Ni$_2$P (10 mg, 30 mL 1.6 mM Na$^{15}$NO$_2$, initially acidified to pH 2, 1 atm H$_2$/Ar, 60 °C, batch reaction). Nitric oxide (NO) hydrogenation in the absence (c) and presence (d) of Ni$_2$P (30 mL deionized water, 1 atm NO/H$_2$, 60 °C) (see Experimental). (pH values in parenthesis)

The change in product selectivity from NH$_4^+$ to N$_2$ when switching the initial hydrogenation reactant from NO$_3^-$ to NO$_2^-$ has important practical implications. Forming N$_2$ requires an entropically difficult, bimolecular step where two reactive N-species must come together on the catalyst surface. Prior work on bimetallic catalysts has indicated that higher concentrations of NO$_2^-$ intermediate increase the selectivity for N$_2$.\textsuperscript{73,74} In our experiments above, the effective concentration of NO$_2^-$ is obviously much higher during NO$_2^-$ hydrogenation than during NO$_3^-$ hydrogenation, which helps explains the observed selectivity. Critically, the small, steady state concentration of NO$_2^-$ intermediate during NO$_3^-$ hydrogenation must depend on the active surface, and must thus be susceptible to tuning through catalyst modification.
Similar to NO$_x$ and NO$_2$, NO is also hydrogenated in the presence of Ni$_3$P. However, this reaction is more complicated and less selective compared to the former two, in part because even in the absence of catalyst, NO can disproportionate—into NO$_x$ and NH$_4^+$ products—and/or become oxidized—to NO$_2$—by leftover O$_2$ in aqueous solution. Based on our results, we conclude that both NO$_2$ and NO are competent intermediates in NO$_2$ hydrogenation over Ni$_3$P (Scheme 1b).

**Surface chemistry and cocatalyst effects.** Because catalytic activity depends on surface chemistry, we measured and compared the X-ray photoelectron spectroscopy (XPS) of Ni$_3$P at different stages of synthesis, activation, and catalysis. As made, H$_2$-annealed, and post-catalysis ("1 cycle") Ni$_3$P each show signals corresponding to two main Ni and two main P species (Figure 5). In all samples, the Ni 2p$_{3/2}$ region shows a main peak at a binding energy of 853.0 eV—slightly higher than that of Ni$^{0}$ (852.6 eV)—which is consistent with previous reports for the very small positive charge (Ni$^{\delta+}$) in Ni$_3$P (Table 2). Another smaller peak—at 853.6 eV for as made Ni$_3$P, and at 855.7 eV for H$_2$-annealed and 1 cycle Ni$_3$P (post-catalysis)—corresponds to oxidized Ni$^{2+}$; interestingly, the former is normally associated with NiO, while the latter is with Ni(OH)$_2$. In all samples, the P 2p region also exhibits two peaks, a main one at 129.1 eV corresponding to phosphide (P$^3$) in Ni$_3$P, and another smaller peak at 133.2 eV characteristic of a fully oxidized phosphorous species (P$^{5+}$), most likely PO$_4^{3-}$.

**Table 2.** Selected XPS measurements of Ni$_3$P nanocrystals used in catalytic nitrate (NO$_3^-$) hydrogenation.

<table>
<thead>
<tr>
<th>Assignment, energy (eV)</th>
<th>As made Ni$_3$P</th>
<th>H$_2$-anld. Ni$_3$P</th>
<th>Ni$_3$P 1 cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$^{2+}$ 2p$_{3/2}$</td>
<td>40%</td>
<td>34%</td>
<td>32%</td>
</tr>
<tr>
<td>853.0(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni$^{2+}$ (NiO) 2p$_{3/2}$</td>
<td>4%</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>853.6(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni$^{2+}$ (Ni(OH)$<em>2$) 2p$</em>{3/2}$</td>
<td>na</td>
<td>3%</td>
<td>3%</td>
</tr>
<tr>
<td>855.7(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P$^3$ 2p$_{3/2}$</td>
<td>68%</td>
<td>57%</td>
<td>63%</td>
</tr>
<tr>
<td>129.1(4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P$^{5+}$ 2p$_{3/2}$</td>
<td>32%</td>
<td>43%</td>
<td>37%</td>
</tr>
<tr>
<td>133.2(7)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Calibrated using C 1s peak at 284.6 eV as reference. Assignments agree with NIST XPS database as well as with previous reports.$^{53,56}$ P 2p$_{3/2}$ - P 2p$_{1/2}$ spin-orbit splitting $\Delta=0.87$ eV, P 2p$_{3/2}$ overlaps P 2p$_{1/2}$.

Interestingly, both of the relative amounts of oxidized Ni (Ni$^{2+}$) and P (PO$_4^{3-}$) species on the Ni$_3$P surface increase after annealing, and remain similarly high after catalysis (Table 2). We explain these observations as follows: After initial synthesis, as made Ni$_3$P nanocrystals contain small amounts of NiO impurity on their surface.$^{79}$ During activation, H$_2$ annealing removes this NiO impurity, specifically by reducing it to a small, relatively amorphous—XRD silent—amount of zerovalent (metallic) Ni$^{0}$, or more Ni$^{\delta+}$. However, these latter species—surface Ni$^{0}$ or Ni$^{\delta+}$—are relatively reactive, and quickly transform into Ni(OH)$_2$ upon exposure to air before XPS measurements are made. Similarly, some Ni(OH)$_2$ and PO$_4^{3-}$ species may form by exposure of surface sites upon removal of surface passivating ligands during H$_2$ annealing.$^{51,57}$ Annealing makes the Ni$_3$P surface much more reactive, and also more susceptible to oxidation—by air or moisture—during handling and characterization.

**Figure 5.** XPS of as made, H$_2$-annealed (activated), and recycled (after 1 cycle) Ni$_3$P showing the Ni 2p$_{3/2}$ (a) and P 2p$_{3/2}$ (b) regions.

**Figure 6.** NO$_3^-$ hydrogenation over Ni$_3$P vs Ni (a). NO$_3^-$ hydrogenation over Ni$_3$P with equimolar amounts of Ni(II) (b). PO$_4^{3-}$ and both sources added (c) (10 mg, 30 mL 2 mM NaNO$_3$, initially acidified to pH 2, 1 atm H$_2$/Ar, 60 °C, see Experimental).
To test whether the observed Ni$^{2+}$ and PO$_4^{3-}$ species contribute—either separately or together—to NO$_3^-$ hydrogenation, we repeated our catalytic experiments in the presence of sources of Ni$^{2+}$ or PO$_4^{3-}$ or both ions, in addition to Ni$_2$P (Figure 6). Compared to the Ni$_2$P only-catalyzed reaction, adding NiO decreased NO$_3^-$ hydrogenation activity by 35%, while adding Ni(OH)$_2$ decreased it by 62%. In turn, adding Na$_3$PO$_4$ decreased NO$_3^-$ hydrogenation activity by 63%, while adding Ni$_3$$(PO_4)_2$ decreased it by 71%. Because either or both Ni(II) and P(V) sources added on purpose clearly hinder and reduce catalytic activity, we conclude that these impurities, which are observed by XPS, do not contribute or act as cocatalysts in NO$_3^-$ hydrogenation.

Finally, we probed whether a small amount of undetected Ni$^0$ could be responsible for the NO$_3^-$ hydrogenation results shown here. To do this, we compared the activity and selectivity of nanocrystalline Ni$_2$P with that of Ni made independently, after each of them was annealed and activated in the same way under H$_2$ (see Experimental). At 1 atm H$_2$ and 60 °C for 4 h, a 2 mM solution of NO$_3^-$ is almost completely hydrogenated, down to 0.02 mM (99% conversion) over Ni$_2$P, with a very high selectivity for NH$_4^+$ (96%) (Figure 6a). In contrast, under identical reaction conditions, the same solution is only slightly hydrogenated, down to 1.7 mM NO$_3^-$ (17% conversion) over Ni, without producing any measurable NH$_4^+$. It is known that Ni reacts with HNO$_3$ to give gaseous nitrogen oxides such as nitric oxide (NO).$^{23,80}$ Because Ni is much less reactive, and because it has a very different selectivity toward NO$_3^-$ hydrogenation compared to Ni$_2$P, we conclude that any traces of metallic (zerovalent) Ni, if present, cannot be responsible for the reactivity observed with Ni$_2$P.

**Insights from computations: gas vs. liquid phase.** Using DFT (VASP, PBE, see Experimental) we calculated the change of energy $\Delta E$ for NO$_3^-$ hydrogenation in the gas phase (Table 3). Each individual reaction step is highly exothermic. Using VASPsol to account for electrostatics, cavitation, and dispersion between solute and solvent, we also calculated $\Delta E$ for NO$_3^-$ hydrogenation in the liquid phase (Table 3). These results strongly indicate that the individual NO$_2^-$ hydrogenation step becomes least exothermic and, in the absence of appropriate conditions, somewhat more difficult. It is possible to combine NO$_2^-$ and NO hydrogenations into a single step (last entry, Table 3) but, because this requires breaking two H$_2$ bonds, it may be kinetically difficult. Therefore, these calculations point to nitrite (NO$_2^-$) being the most likely bottleneck step in nitrate (NO$_3^-$) hydrogenation in the absence of a suitable catalyst.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta E_g^{a}$ (eV)</th>
<th>$\Delta E_l^{b}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$ + H$_2$ $\rightarrow$ NO$_2^-$ + H$_2$O</td>
<td>-1.12</td>
<td>-1.57</td>
</tr>
<tr>
<td>NO$_2^-$ + H$_2$ $\rightarrow$ NO$^+$ + H$_2$O</td>
<td>-0.41</td>
<td>-0.22</td>
</tr>
<tr>
<td>NO$^+$ + H$_2$ $\rightarrow$ H$_2$NO$^-$</td>
<td>-0.68</td>
<td>-0.98</td>
</tr>
<tr>
<td>H$_2$NO$^-$ + H$_2$ $\rightarrow$ NH$_2$ + H$_2$O</td>
<td>-1.50</td>
<td>-1.95</td>
</tr>
<tr>
<td>NO$_2^-$ + 2H$_2$ $\rightarrow$ H$_2$NO$_2^-$ + H$_2$O</td>
<td>-1.05</td>
<td>-1.20</td>
</tr>
</tbody>
</table>

$^a$Gas phase energy change. $^b$Liquid phase energy change.

**Table 3.** Calculated energy changes for different steps of nitrate (NO$_3^-$) hydrogenation.
Ni$_2$P(001) surface reconstruction. The PBE calculated surface lattice constants (\(a\)) of Ni$_2$P(001) and fcc Ni(111) are 5.872 Å and 2.488 Å, respectively. Thus, the surface unit cell of Ni$_2$P(001) is ca. 5.6 times larger than that of Ni(111). Along the (001) direction, the Ni$_2$P unit cell has a bilayer structure, with three Ni and two P atoms in one plane, and three Ni and one P atom in the other. Cutting a Ni$_2$P crystal along the (001) direction thus generates two types of surface terminations: a Ni-rich or “Ni$^+$” surface (Figure 7a), and a P-rich or “Ni$^-$P$^+$” surface (Figure 7b). Using DFT, we determine that a large variety of adsorbates (H, O, N, NO) induce a reconstruction of the Ni-rich surface (Figure 7c). This reconstruction involves the surface layer as well as atoms deeper in the structure. First, the three Ni atoms surrounding one of the P atoms on the second layer move closer to each other, allowing the second P atom on the second layer to move up to the top layer. Thus, the top layer has a similar chemical composition to the P-rich termination, but rotated by 30°. The P atoms directly beneath the one that has already moved also move up. In total, almost half of the P atoms move up. When the thickness of the slab is larger than 3 bilayers, this restructuring remains stable after removal of the adsorbate. In vacuum, the reconstructed surface is about 0.09 eV more stable than the unreconstructed structure and, in solution, it is about 0.05 eV more stable. We also note that the clean Ni-rich termination, although unstable towards reconstruction, is metastable. DFT calculations show that H atoms only induce reconstruction locally.

![Figure 7](image)

Figure 7. (a-c) Different terminations of the Ni$_2$P(001) surface: (a) Ni-rich or “Ni$^+$P$^+$” surface, (b) P-rich or “Ni$^-$P$^+$” surface, and (c) reconstructed Ni-rich surface. The three Ni atoms in each P-rich surface unit cell are close to each other, forming a local configuration resembling that of the Ni(111) surface, while the Ni atoms in the Ni-rich surface unit cell are more open. (d-f) Top view of H adsorption on Ni$_2$P surfaces: (d) 1 H, (e) 2 H, (f) 3 H per unit cell (see Table 4). Ni: green; P: gold; H: (small) white.

Hydrogen adsorption. Figure 7d-f, Table 4, and Figure 8 show DFT calculations for the hydrogen adsorption on the Ni-rich terminated surface. Because of the aforementioned reconstruction, the results are similar to that with P-rich termination. On the Ni-rich surface, the adsorption energies per H atom with a vacuum interface are -0.60 eV, -0.27 eV and -0.15 eV with 1, 2, and 3 H atoms in a single unit cell, respectively. This corresponds to -0.70 eV, -0.35 eV, and -0.17 eV, respectively, for the P-rich surface. At low coverage on the P-rich surface, with 1 H adsatom in each unit cell, the adsorption energy is about -0.70 eV, but with 2 or 3 H adatoms in each unit cell, adsorption becomes much weaker. In other words, in the presence of H$_2$ (gas), increasing the hydrogen coverage above 1 H per unit cell does not decrease the total energy. Thus, the calculated hydrogen saturation coverage on Ni$_2$P(001) is about 1 H per unit cell, or ca. 3 nm$^{-2}$. This is in sharp contrast to what is observed for either Pd(111) and Ni(111), where there are very weak interactions between H adatoms separated \(\sqrt{3}\) or more lattice constants. In these cases, and without even considering subsurface adsorption, the hydrogen saturation coverage is ca. 15-18 nm$^{-2}$.

Table 4. Select adsorption energies (eV) on different metal surfaces.

<table>
<thead>
<tr>
<th></th>
<th>Ni$_2$P (001)</th>
<th>Ni (111)</th>
<th>Pd (111)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>-0.72</td>
<td>-0.59</td>
<td>-0.63</td>
<td>H$_2$(g)</td>
</tr>
<tr>
<td>Vacuum</td>
<td>-0.70</td>
<td>(r7x7)</td>
<td>(r7x7)</td>
<td></td>
</tr>
<tr>
<td>1 H$^a$</td>
<td>-0.36</td>
<td>-0.59</td>
<td>-0.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2x2)</td>
<td>(2x2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 H$^a$</td>
<td>-0.18</td>
<td>-0.58</td>
<td>-0.62</td>
<td>NO$_3$(g)</td>
</tr>
<tr>
<td></td>
<td>(r3x3)</td>
<td>(r3x3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO$_3$</td>
<td>-2.40</td>
<td>-2.24</td>
<td>-1.78</td>
<td>NO$_2$(g)</td>
</tr>
<tr>
<td></td>
<td>(2x2)</td>
<td>(2x2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO$_2$</td>
<td>-2.17</td>
<td>-1.97</td>
<td>-1.64</td>
<td>NO(g)</td>
</tr>
<tr>
<td></td>
<td>(2x2)</td>
<td>(2x2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>-2.32</td>
<td>-2.48</td>
<td>-2.30</td>
<td>NO(g)</td>
</tr>
<tr>
<td></td>
<td>(2x2)</td>
<td>(2x2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Number of H per Ni$_2$P unit cell area. Unit cells for fcc(111) metal calculations (with 1 H per unit cell) are chosen to roughly cover the same regime of H coverage (per unit area) as on Ni$_2$P.

Our results agree with prior computational studies, which found that the total adsorption energy is similar when the coverage is doubled (or tripled) on Ni$_2$P(001), but roughly doubles (triples) for Pd(111) and Ni(111) for the selected coverage range (using a larger supercell). The same study explained the enhanced activity of Ni$_2$P toward HER based on a smaller barrier for recombination and desorption of H$_2$ on Ni$_2$P relative to Pd and Ni.

Unlike the case for H, the calculated adsorption energies of nitrogen-based oxyanions, encased explicitly within water clusters and with their charge balanced by H$_2$O$^+$ do
not show significant differences across the three different metal surfaces (see S.I.). In Table 4, we listed the adsorption energies of an initially neutral NO₃ molecule on various surfaces, which show similar behavior. Therefore, a new possible explanation for the enhanced hydrogenation ability of Ni₃P observed here is that, because its hydrogen (H) saturation coverage is much lower than that of other metals, Ni₃P retains enough surface sites available for coadsorption of NO₃. In contrast, the surface of pure Pd and Ni is almost completely covered by H, and the adsorption of NO₃ is especially difficult.

![Figure 8](image-url) Adsorption energy as a function of H coverage for (a) Ni₃P(001) in vacuum, (b) Ni₃P(001) in water, and (c) Ni(111) and (d) Pd(111) in vacuum.

CONCLUSIONS

In summary, nitrate is quickly hydrogenated under relatively mild conditions (1 atm H₂, 60 °C, acidic pH) in the presence of activated Ni₃P nanocrystals. The reaction produces ammonia (NH₃) with very high selectivity (96%), a relatively rare feature shared by only a sliver of known nitrate hydrogenation catalysts. This is also one of the first observations of nitrate hydrogenation with a non-noble-metal catalyst, and its high selectivity toward ammonia allows to envision a process by which nitrate, a pollutant, could be recycled back to more useful fertilizer.

Unlike bimetallic catalysts, single phase Ni₃P is capable of completely reducing nitrate beyond the nitrite (NO₂⁻) stage. This is confirmed by separate experiments where nitrite hydrogenation was used as reactant. Interestingly, the selectivity changed from mostly NH₃ to NH₄⁺ for nitrite hydrogenation, to a mixture of NH₃ and N₂—for nitrite hydrogenation. Because product selectivity is linked to the local concentration of nitrite on the catalyst surface, we believe other metal phosphide nanophases may enable to purposely tune the hydrogenation selectivity toward N₂.

Usually inert alkylsulfonate buffers react with Ni₃P under hydrogenation conditions, suggesting that other tough hydrogenation reactants, including polluting oxyanions and oxysalts (ClO₄⁻, SO₄²⁻, etc.) could also be chemically removed by Ni₃P-mediated hydrogenation. A self-sustaining, hydrogen-free photocatalytic nitrate reduction in the absence of sacrificial agents may also be envisioned. Neither Ni(II) nor P(V) species, which are observed by XPS appear to have an effect on nitrate hydrogenation. Nor does zerovalent Ni, which may be present as a small amorphous impurity after activation by H₂ annealing. A small yet measurable decrease in activity after 4 consecutive cycles, perhaps due to partial etching or re-passivation (fouling) of the Ni₃P surface, may be prevented by either immobilization on a support, or by reactivation (H₂-reannealing), respectively.

The Ni₃P(001) surface has a smaller density of surface Ni atoms than the Ni(111) surface. DFT shows that the reconstructed Ni-rich and P-rich surfaces display ensembles of Ni atoms that locally resemble the Ni(111) surface. The unreconstructed Ni₃P surface, having unfavorable H adsorption may be inactive. However, treatment with H₂ and other adsorbates results in reconstruction and activation. Alternatively, because Ni₃P(001) has an H saturation density that is about 1/3 to 1/4 smaller than that of Ni(111) and Pd(111), the former may be better able to accommodate the binding of otherwise very weakly coordinating nitrate ions, while the latter two may not. In addition to advancing the scope of important hydrogenations catalyzed by Earth abundant transition metal phosphides, this work will help in improving our understanding the basic science behind catalytic nitrate hydrogenation and, in turn, advancing the next generation of technologies for the safe and effective removal of nitrate from water.

EXPERIMENTAL

Materials. Triphenylphosphite (P(OPh)₃, 97%) and nickel(II) acetylacetonate hydrate (Ni(acac)₂·H₂O) were purchased from Strem; nickel(II) acetate tetrahydrate (Ni(OAc)₂·4H₂O, ≥99.0%), mesoporous silica (SiO₂, SBA-15), oleylamine (technical grade, 70%), 1-octadecene (ODE, technical grade, 90%), and sodium nitrite (NaNO₂, 99.9999%) from Sigma; palladium chloride (PdCl₂·H₂O) from D. F. Goldsmith; copper nitrate (Cu(NO₃)₂·3H₂O, 99%), sulfuric acid (H₂SO₄, certified ACS plus), hydrochloric acid (HCl, certified ACS plus), sodium nitrate (NaNO₃, certified ACS), acetone, and toluene (99.9%) from Fisher; hydrogen gas (H₂) and argon gas (Ar) from Airgas; nitric oxide (NO, 99%) from Praxair; Na⁵¹NO₂ (98% ¹⁵N-labeled) is from Cambridge Isotope Laboratories. Colorimetric kits (0.10-25.0 mg/L NO₃⁻; 0.002-1.00 mg/L NO₂⁻; 2.0-150 mg/L NH₄⁺) were purchased from Merck. All chemicals were used as received. MilliQ water is used all over the experiments.

Synthesis. Ni₃P, Ni(OAc)₂·4H₂O (0.36 mmol, 90 mg), oleylamine·H₂O (5 mmol, 1.35 g, 1.66 mL), and ODE (5 g, 6.34 mL) were degassed under a vacuum at 80 °C for 1 h, refilled with Ar, then heated to 275 °C. The mixture was heated to 275 °C, 0.55 mL of P(OPh)₃ was injected, the temperature maintained while stirring for 30 min. The mixture was...
cooled to room temperature (21 °C, R.T.), and solids were isolated and washed twice with toluene by centrifugation at 4500 rpm for 3 min. Ni(acac)₂ (7.8 mmol, 2 g) and oleyl amine (78 mmol, 20.8 g, 25.6 mL) were degassed under dynamic vacuum at 100 °C for 1 h. The mixture was refilled with dry Ar and heated to 220 °C for 2 h. After cooling to R.T., 40 mL acetone were added. Solids were isolated by centrifugation at 4500 rpm for 5 min. Pd-Cu/SiO₂ was annealed at 400 °C for 1 h under a flow of H₂/Ar (1 atm). Pd-Cu/SiO₂ was annealed at 450 °C for 2 h under a flow of H₂/Ar.

Characterization. UV-Vis absorption spectra were collected with a photodiode-array Agilent 8453 UV-Vis Spectrometer. Powder X-ray diffraction (XRD) was performed using a Rigaku Ultima IV diffractometer with a Cu Kα radiation (40 kV, 44 mA). X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Amicus/ESCA 3400 instrument. The sample was irradiated with 240 W monochromated Mg Kα X-rays, and photoelectrons emitted at 0° from the surface were energy analyzed using a DuPont type analyzer. The pass energy was set at 150 eV. CasaXPS was used to process raw data files. The binding energy of C 1s at 284.6 eV was used as a reference. Transmission electron microscopy imaging was performed on an FEI Tecnai G2 F-20 scanning transmission electron microscope. Gas chromatography-mass spectrometry was acquired on an Agilent 7250 GC Q-TOF. Dynamic light scattering (DLS) was performed on a Malvern Zetasizer Nano ZS.

Catalytic Hydrogenation. 10 mg dry catalyst were placed in a 3-neck round bottom flask. A solution of NaN₃ or NaN₂ in deionized water (30 mL), previously sparged with Ar for 15–20 min, and with a pH adjusted by the addition of either HCl or H₂SO₄ was added. A 5-10% mixture of H₂ in Ar was flowed at a rate of ca. 5 mL/min while vigorously stirring at a rate of (700-1200 rpm) and a temperature at 60 °C. When NaN₃ was used, the reaction was simply filled with H₂/Ar and run in batch (closed) to facilitate analysis of the headspace (100 mL) by GC analysis. When NO was used, a NO:H₂ mixture was used. pH control and recyclability. To maintain a constant acidic pH, a solution of either HCl or H₂SO₄ was continuously added during the cycle via syringe pump. Similarly, to start a new cycle, a small aliquot of a concentrated NaN₂ solution was re-introduced. NO₂⁻, NO₃⁻, and NH₄⁺ Quantification. Colorimetry methods were used to determine the aqueous concentrations of NO₃⁻, NO₂⁻, and NH₄⁺.

Calculations. Density functional Theory (DFT) calculations of the total energies were performed using the VASP package (v.5.4) with the standard PAW potentials and the PBE functional. The energy cutoff of the plane-wave basis sets is 400 eV. The bulk Ni₃P crystal is hexagonal (space group P₆₃mc No. 189), with 6 Ni and 3 P atoms in each supercell. The theoretical lattice constants obtained from energy minimization are a = b = 5.872 Å, and c = 3.369 Å. The Ni₃P(001) surface was modeled by periodic arrays of slabs separated by 12 Å of vacuum. Reactions were adsorbed on one side (the top) of the slab. Both adsorbates and the substrate atoms are allowed to relax, with the exception of the bottom layer of atoms which were fixed at their bulk positions. The Brillouin zone was sampled using a (12x12x1) grid. All energetics reported were average values of results using 4 to 7 bilayers of substrates. Most of the calculations were performed with the standard VASP code that is most applicable to gas-solid interface. Some calculations were also performed using VASPsol which includes the effect of electrostatics, cavitation, and dispersion between a solute and solvent.

ASSOCIATED CONTENT
Supporting Information. Additional structural characterization, catalysis and conversion data, control experiments, and computational details are shown in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org

AUTHOR INFORMATION
Corresponding Author
*vela@iastate.edu

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REFERENCES


TOC Figure