

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

Scheme 1. (a) Catalytic NO_3^- hydrogenation and (b) some of its common intermediates.

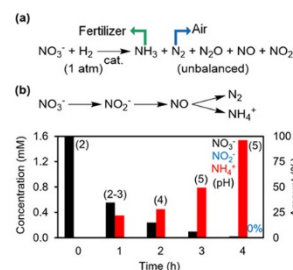


Figure 1. Aqueous nitrate (NO_3^-) hydrogenation over H_2 -annealed (activated) Ni_2P nanocrystals (10 mg, 30 mL 1.6 mM NaNO_3 , initially acidified to pH 2, 1 atm H_2/Ar , 60 °C). (pH values in parenthesis)

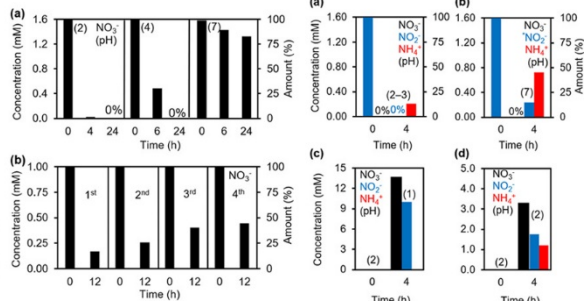


Figure 2. (a) Effect of pH on NO_3^- hydrogenation activity over Ni_2P . (pH values in parenthesis) (b) Consecutive NO_3^- hydrogenation runs over recycled Ni_2P at pH 3 (10 mg, 30 mL 1 mM NaNO_3 , 1 atm H_2/Ar , 60 °C).

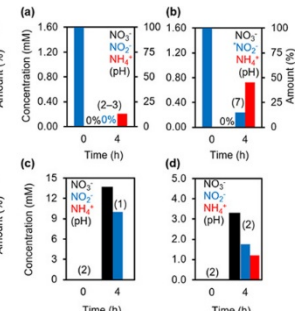


Figure 3. (a) Nitrite (NO_2^-) hydrogenation over Ni_2P (10 mg, 30 mL 1.6 mM NaNO_2 , initially acidified to pH 2, 1 atm H_2/Ar , 60 °C). (b) $^{15}\text{NO}_2^-$ hydrogenation over Ni_2P (10 mg, 30 mL 1.6 mM $\text{Na}^{15}\text{NO}_2$, initially acidified to pH 2, 1 atm H_2/Ar , 60 °C, batch reaction). Nitric oxide (NO) hydrogenation in the absence (c) and presence (d) of Ni_2P (30 mL deionized water, 1 atm NO/H_2 , 60 °C). (pH values in parenthesis)

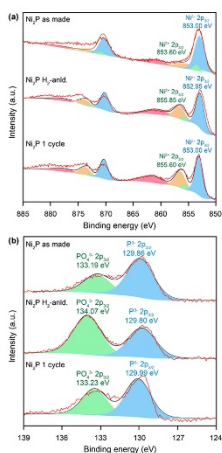


Figure 4. XPS of as made, H_2 -annealed (activated), and recycled (after 1 cycle) Ni_2P nanocrystals showing the Ni $2p_{3/2}$ (a) and P $2p$ (b) regions.

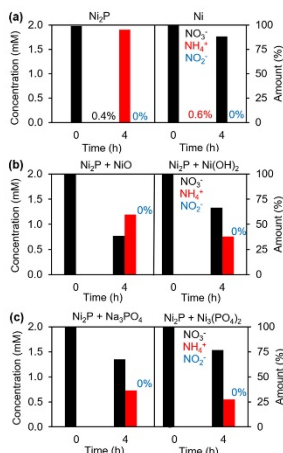


Figure 5. NO_3^- hydrogenation over Ni_2P vs. Ni (a). NO_3^- hydrogenation over Ni_2P with equimolar amounts of Ni(II) (b). PO_4^{3-} and both sources added (c) (10 mg, 30 mL 2 mM NaNO_3 , initially acidified to pH 2, 1 atm H_2/Ar , 60 °C).

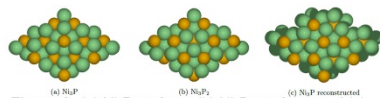


Figure 6. (a) Ni_2P surface, (b) Ni_3P_2 surface, and (c) reconstructed Ni-rich surface.

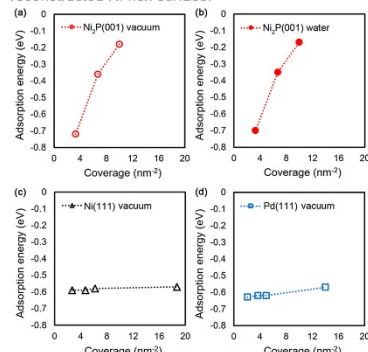


Figure 7. Adsorption energy as a function of H coverage for (a) $\text{Ni}_2\text{P}(001)$ in vacuum, (b) $\text{Ni}_2\text{P}(001)$ in water, and (c) Ni(111) and (d) Pd(111) in vacuum.

Outcome. Nitrate is quickly hydrogenated under relatively mild conditions (1 atm H_2 , 60 °C, acidic pH) in the presence of activated Ni_2P nanocrystals. This is one of the first observations of nitrate hydrogenation with a non-noble-metal catalyst. Published in: *ACS Catal.* **2020**, *10*, 3618–3628,

<https://doi.org/10.1021/acscatal.9b05338>

Impact & Benefits. Access to clean water is an essential prerequisite for communities to prosper. Excess concentration of nitrate is responsible for birth defects (“blue baby” syndrome) and thyroid and bladder cancers. This project allows to remove nitrate efficiently with a non-precious metal-based catalyst at near ambient conditions. The reaction is highly selective toward ammonia (NH_3), a potentially reusable form of nitrogen.

Background & Explanation. This project was led by chemistry graduate students Lin Wei and Bryan A. Rosales, chemistry professor Javier Vela, and collaborators from Iowa State University and the Ames Laboratory. This work will help improving understanding the basic science behind nitrate hydrogenation and advancing the next generation of technologies for the safe and effective nitrate removal.