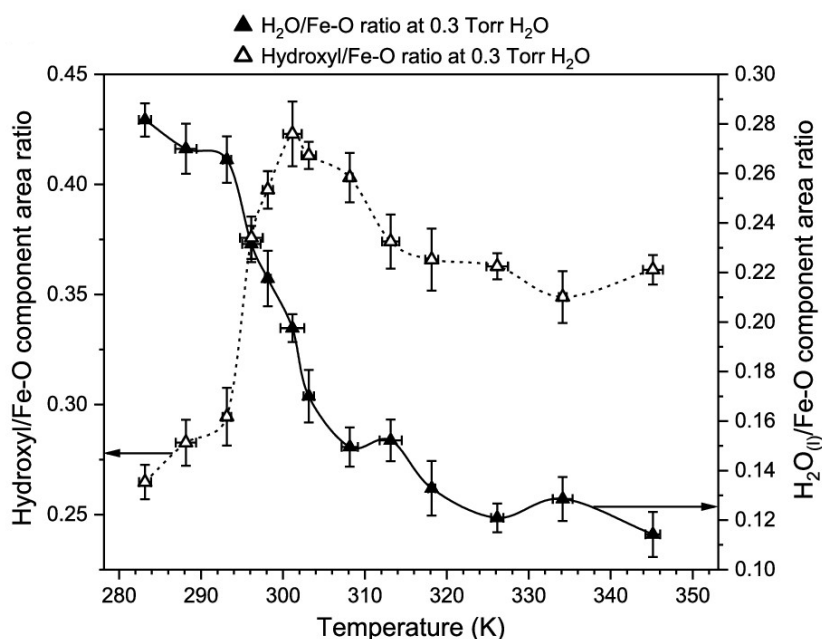
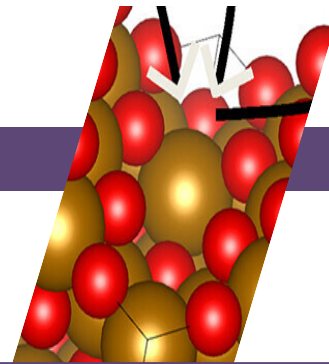


From Magnetite to Ammonia, A New Line of Production



The ratios of surface hydroxyl (open symbols) and water (closed symbols) relative to Fe–O magnetite nanoparticles change with temperature after exposure to water vapor. The hydroxylated magnetite lowers the barrier to nitrogen gas (N_2) interaction and reduction and thus results in the formation of ammonia and hydrazine.

Toward a more efficient path to ammonia

Agriculture depends on ammonia, a critical ingredient in most fertilizers. Chemical manufacturing also relies on ammonia for various processes, from the production of pharmaceuticals to cleaning agents.

Outside of lightning strikes, decomposition, and specialized bacteria, ammonia does not readily form in nature. The Haber–Bosch process is the main industrial process for ammonia production. It typically uses hydrogen from fossil sources, requires very high temperatures and pressures, and is a large source of carbon dioxide emission.

Recent experiments have suggested that magnetite (Fe_3O_4) nanoparticles in the presence of microdroplets of water and nitrogen gas under near-ambient conditions offer an alternate process to create ammonia. Until recently the mechanism behind this process remained unclear. This new study provides the first direct spectroscopic evidence of surface hydroxylation (water splitting) and nitrogen adsorption in the production of ammonia.

Beamline data agrees with theoretical predictions

Researchers from two divisions within Lawrence Berkeley National Laboratory

Scientific Achievement

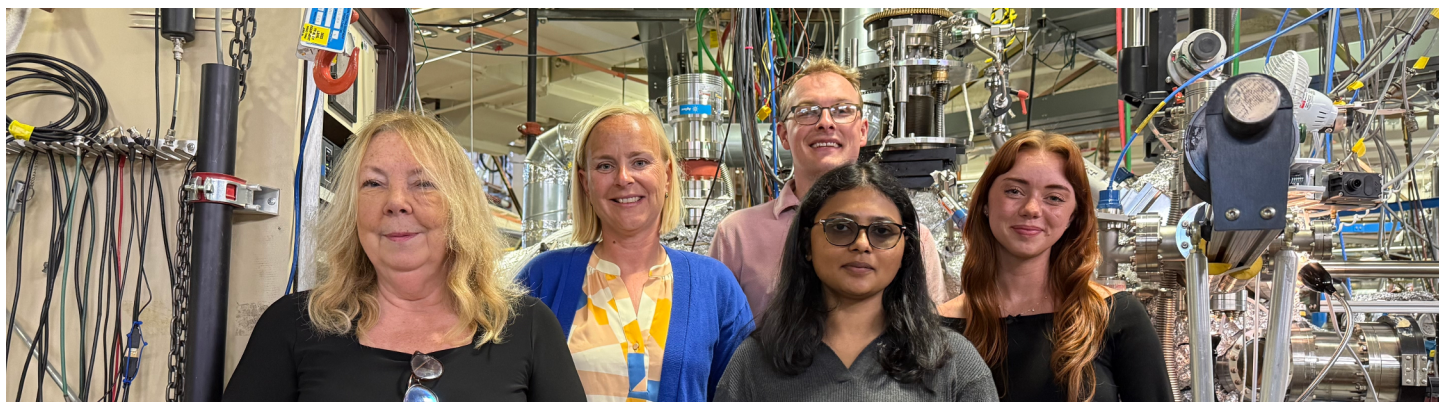
Researchers studied a novel approach to ammonia synthesis by measuring the surface hydroxylation of magnetite nanoparticle catalysts under ambient, in situ conditions at the Advanced Light Source (ALS).

Significance and Impact

These experimental and modeling results pave the way for more efficient and economical ammonia production.

(Berkeley Lab)—the ALS and the Chemical Sciences Division—collaborated to combine ambient-pressure x-ray photoelectron spectroscopy (APXPS) data from the ALS with ab initio computational methods to clarify the role of hydroxylation and active surface sites on magnetite nanoparticles that enable nitrogen reduction.

The team used APXPS at two ALS beamlines. Beamline 9.3.2, which produces low-energy, soft x-rays, exposed magnetite nanoparticles placed on gold foil to varying pressures of water vapor and nitrogen gas, as well as different temperatures. Under these experimental conditions, the team aimed to understand



From left to right: Teresa Head-Gordon, Moni Blum, Shane Devlin, Sruthy Kettidathil Chandy, and Nykita Rustad analyzed samples at Beamlines 9.3.1 and 9.3.2 at the Advanced Light Source. (Credit: Erika Riffe/Berkeley Lab)

hydroxyl formation on the nanoparticle surface by measuring the core level spectra of iron, nitrogen, oxygen, and carbon. The team used Beamline 9.3.1, which offers medium-energy, tender x-rays, to expose the samples to higher photon excitation and thus allowed to increase the water vapor and nitrogen gas pressures during the experiments.

In parallel, the team conducted advanced quantum chemistry-based simulations that clarified how water molecules split and create special surface sites on the magnetite nanoparticles. The sites provide locations where the nitrogen reduction takes place. Ab initio molecular dynamics and free energy calculations also confirmed that hydroxylated magnetite surfaces lower energetic barriers for nitrogen reduction, which enables diverse binding geometries and proton-coupled electron transfer mechanisms.

A mechanism explained

This is the first study to provide an integrated experimental-theoretical foundation for understanding the atomic-scale mechanism behind ammonia synthesis at water-magnetite interfaces

that drive nitrogen fixation under ambient conditions, a longstanding goal of sustainable chemistry. This new approach shifts the paradigm from viewing nitrogen binding as a rate-limiting step that hinders ammonia production to recognizing that water activation can

enable and enhance catalytic activity. This insight can guide future efforts for ammonia synthesis with low energy input and minimal carbon emissions.

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