

# Water-durable perovskite-oxynitride supported nickel catalysts for ammonia decomposition

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## Novel Barium Titanate Oxynitride-Supported Ni Catalysts for Ammonia Decomposition

Nickel (Ni) is a promising alternative to ruthenium for hydrogen production via ammonia (NH<sub>3</sub>) decomposition

However, the weak nitrogen affinity of Ni at low temperatures affects its hydrogen production efficiency

Catalyst

H<sub>2</sub>

**Water-durable hexagonal barium titanium oxynitride (h-BaTiO<sub>3-x</sub>N<sub>y</sub>)-supported Ni catalysts**

**Non-noble metal catalyst Ni/h-BaTiO<sub>3-x</sub>N<sub>y</sub>**

Mars-van Krevelen type mechanism

O<sup>2-</sup> substituted by N<sup>3-</sup> ions

Operation temperature lowered by over 140 °C

<sup>15</sup>NH<sub>3</sub> decomposition reaction + FT-IR measurements

N<sup>3-</sup> vacancies act as active sites

**The proposed catalyst:**

Outperforms conventional oxide-supported Ni catalysts

Exhibits catalytic activity higher than that of Ni/h-BaTiO<sub>3-x</sub>H<sub>y</sub>

Maintains activity after exposure to water

**Substituting N<sup>3-</sup> ions at oxygen sites is effective for the development of novel catalysts for ammonia decomposition**

Ammonia decomposition over water-durable hexagonal BaTiO<sub>3-x</sub>N<sub>y</sub>-supported Ni catalysts

Ogasawara et al. (2023) | *Advanced Energy Materials*

Substituting  $N_3^-$  ions at oxygen sites is effective for the development of novel catalysts for ammonia decomposition. Credit: Tokyo Tech

Hydrogen has become the beacon of clean energy owing to its high energy density and carbon-free emissions. Despite these advantages, hydrogen fuel is still far from being commercialized. Liquefying hydrogen requires a huge amount of energy and extremely low temperatures, making its large-scale production and transportation over long distances quite challenging.

Fortunately, ammonia is a promising [hydrogen](#) carrier that can be easily liquified under milder conditions, transported, and decomposed with the help of a catalyst to produce pure nitrogen gas and the desired hydrogen gas.

Over the years, studies have found that basic oxide support promotes ammonia [decomposition](#) reaction in the presence of non-noble metal catalysts such as nickel (Ni) by facilitating electron donation. A similar ability to promote ammonia catalysis is seen in nitrogen-containing support materials. While the former requires high operating temperatures for catalysts, the latter is highly sensitive to air and water, which can lead to an irreversible deactivation.

In a recent breakthrough published in *Advanced Energy Materials*, a team of researchers led by Professor Masaaki Kitano from Tokyo Institute of Technology (Tokyo Tech) has overcome these hurdles by developing a highly active Ni-based ammonia decomposition catalyst supported on hexagonal barium titanium oxynitride ( $h\text{-BaTiO}_{3-x}\text{N}_y$ ).

The new precious metal-free catalyst exhibited an excellent ammonia decomposition rate at operating temperatures lower than that required for conventional Ni-based catalysts. "Precious metals like ruthenium are commonly used as ammonia decomposition catalysts but are highly expensive. This study presents a Ni-based alternative that shows a good hydrogen production rate at [low temperatures](#), a feat rather difficult to achieve owing to the weak affinity of nitrogen towards Ni below a certain temperature," explains Prof. Kitano.

In their study, the team explored perovskite-type oxynitrides—a class of materials known for their stability and ability to form nitrogen vacancies. But they have not been exploited as support materials for ammonia decomposition catalysis at [lower temperatures](#) so far.

Here, the researchers synthesized the new Ni/h-BaTiO<sub>3-x</sub>N<sub>y</sub> catalyst by reacting nitrogen gas and Ni/h-BaTiO<sub>3-x</sub>H<sub>y</sub> oxyhydride under mild conditions. The obtained catalyst was then subjected to ammonia decomposition experiments for analyzing its reaction rates and effectiveness.

The team also carried out a series of analytical tests and mathematical calculations to understand its catalysis mechanism.

The results revealed that substituting the O<sup>2-</sup> sites on the BaTiO<sub>3</sub> lattice with N<sup>3-</sup> ions reduced the operating temperature of the Ni-based [catalyst](#) by over 140°C, which significantly outperformed the conventional Ni-based ammonia decomposition catalysts, as well as its oxyhydride precursor.

Furthermore, isotope experiments and Fourier transform-infrared spectroscopy measurements indicated that N<sup>3-</sup> vacancies act as [active sites](#) for the decomposition reaction at the metal support interface, where Ni facilitates the desorption of nitrogen gas from the support. The team

also found that Ni/h-BaTiO<sub>3-x</sub>N<sub>y</sub> was stable in water, and its catalytic activity remained practically unaffected after exposure.

In effect, the study elucidates the catalysis mechanism, highlighting the significance of N<sup>3-</sup> ion substitution in promoting the catalysis of ammonia decomposition. These insights can promote the development of various highly active non-noble metal catalysts composed of nickel, cobalt, and iron. "This will aid in making the production of [hydrogen fuel](#) from [ammonia](#) more feasible, paving the way for cleaner energy and a greener planet," concludes Prof. Kitano.

**More information:** Kiya Ogasawara et al, Ammonia Decomposition over Water-Durable Hexagonal BaTiO<sub>3-x</sub>N<sub>y</sub>-Supported Ni Catalysts, *Advanced Energy Materials* (2023). [DOI: 10.1002/aenm.202301286](https://doi.org/10.1002/aenm.202301286)

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