

## Design of Novel Catalytic Nitrogen Reduction Sites Based on Atomic-Resolution Electron Microscopic Analysis

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Understanding the structure and chemical state of the active sites is important for the development of highly active catalysts. However, it is difficult to conduct the necessary analyses without exposing reduced catalyst to air, which can alter its structure. We have developed a means of loading reduced catalysts into analytical instruments, such as transmission electron microscopes and various spectroscopic detectors, that avoids exposing the catalyst to the air. Using our non-air-exposure analysis technique, we were able to investigate the nitrogen reduction sites of novel ammonia synthesis catalysts and elucidate the synergistic mechanisms between the catalysts' structures and chemical states. These analyses ultimately allowed us to develop catalysts with high activities at the low temperatures needed for ammonia synthesis using renewable energy. We expect that our non-air-exposure analysis technique will become an important tool for the development of novel catalytic reaction processes, particularly those related to the use of ammonia as a hydrogen carrier, which is an important milestone for establishment of a carbon-neutral society.



### Introduction

Design of active sites is essential for the development of highly active catalysts. X-ray diffraction, X-ray absorption spectroscopy, infrared spectroscopy, and Raman spectroscopy are powerful tools for the characterization of heterogeneous catalysts; however, these techniques cannot directly capture the structure and characteristics of the active site because they provide only average information. Transmission electron microscopy (TEM) has the advantage of position-selective observation of targets; however,

in the study of supported catalysts, where the size of the active site is below the nanoscale and the structure is too disordered, electron microscopy has traditionally played only a supplementary role for observing morphology and measuring particle size. In recent years, technological innovations such as increased resolution by using spherical aberration correctors and the ability to conduct highly sensitive elemental analyses by using large-area energy-dispersive X-ray fluorescence (EDX) detectors have greatly improved what can be achieved with TEM. Adding to these innovations, we have developed a

sample-loading technique that allows simultaneous observation of the structure and chemical state of the active sites of heterogeneous supported metal catalysts at the atomic-level.

Recently, hydrogen carriers have attracted attention as means of storing and transporting renewable energy. One such hydrogen carrier is ammonia, because of its high energy density ( $12.8 \text{ GJ m}^{-3}$ ), high hydrogen content (17.6 wt%), ease of liquefaction and suitability for storage and transportation, and the fact that it can be used to produce hydrogen without emission of  $\text{CO}_2$ .<sup>[1]</sup> Ammonia is produced industrially via the Haber-Bosch process using double-promoted iron catalysts. However, the currently available catalysts are all optimized for large-scale processes operating at high temperatures and pressures, meaning their performances are insufficient for processes that are powered by renewable energy and conducted under much milder conditions. Thus, to address the need for novel ammonia synthesis catalysts, we used our non-air-exposure analysis technique to conduct analyses and develop several catalysts with ammonia synthesis activities superior to those of conventional catalysts. Here, we discuss our sample-loading technique and the development of our improved catalysts.

## Outline of our sample-loading technique

In heterogeneous catalysts, active sites are usually formed on the catalyst surface during activation (reduction). However, when these active sites are exposed to air, their structure and chemical state are changed by reaction with atmospheric oxygen and water vapor. For example,  $\text{Ce}^{4+}$  is reduced to  $\text{Ce}^{3+}$  under high-temperature, reductive conditions, but  $\text{Ce}^{3+}$  is extremely sensitive to oxygen and is easily oxidized back to  $\text{Ce}^{4+}$  upon contact with air. Therefore, the state of the active site cannot be analyzed by TEM by using the usual sample preparation method of grinding and grid preparation in air.

To address this issue, we developed an approach that uses a glove box and special airtight sample holder to prevent the catalyst from being exposed to the air (Figure 1). In brief, after activation (reduction), the catalyst is moved to a glove box filled with an inert gas. Once inside the glove box, the catalyst is placed within the airtight receptacle of a special sample holder. The sample holder is then removed from the glove box and loaded into the TEM instrument. This operation allows the activated catalyst to be introduced into the optical tube of the TEM instrument without exposing it to air, and to be observed and analyzed while maintaining its surface structure and state after reduction.

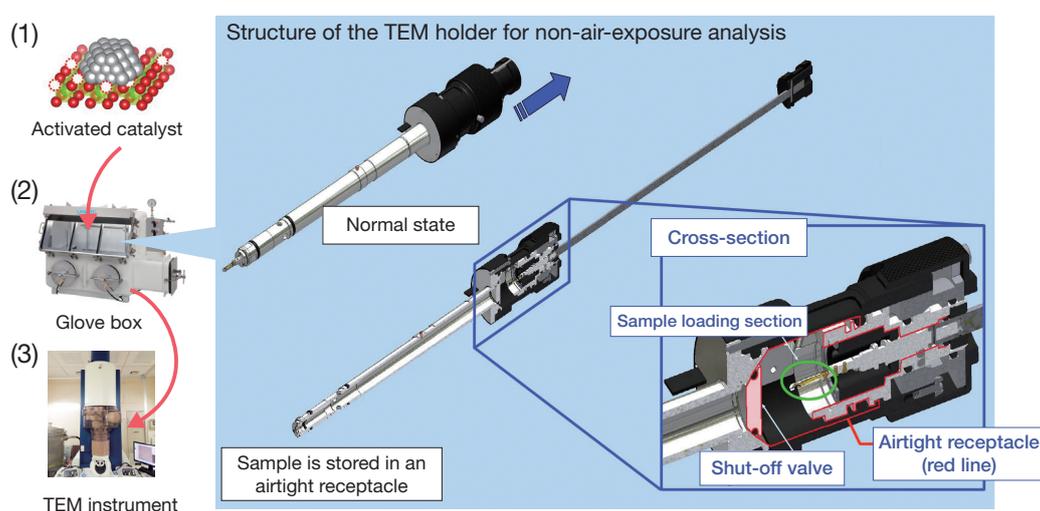


Figure 1 Overview of the sample-loading technique and a schematic showing the structure of the sample holder.  
 (1) The catalyst is activated (reduced) and then moved to a glove box filled with an inert gas.  
 (2) The catalyst is then placed within the airtight receptacle of a special sample holder.  
 (3) The sample holder is then removed from the glove box and inserted into the transmission electron microscope for analysis.

## Example application: Supported Ru catalysts

Under mild conditions, supported ruthenium (Ru) catalysts show higher ammonia synthesis activity than the usual double-promoted iron catalysts.<sup>[1-3]</sup> We developed a cerium-lanthanum composite oxide supported Ru catalyst (Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub>) and found that this catalyst exhibited better activity than conventional supported Ru catalysts; this higher activity was achieved by reducing the catalyst at 650°C, which is a much higher temperature than that used for the reduction of conventional ammonia-synthesis catalysts such as Ru/Cs<sup>+</sup>/MgO and Ru/CeO<sub>2</sub>.<sup>[4]</sup>

Using our non-air-exposure analysis technique, we were able to observe the elemental composition of the surface of the Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub> catalyst by using an EDX detector and to examine the electronic state of Ce by using an electron-energy-loss spectroscopy (EELS) detector (Figure 2). EELS analysis revealed that Ce<sup>3+</sup> was more abundant near the surface of the support (Figure 2c). In addition, detailed analysis of the interface between the Ru nanoparticles and the /La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub> support revealed that it was Ce<sup>+3</sup> rich (Figure 2d, e). The rate-determining step in ammonia synthesis is dissociation of the N<sub>2</sub> molecule. To promote this dissociation, electrons can be donated to N<sub>2</sub> molecules adsorbed on the catalyst surface. Our analysis indicated that Ru adjacent to Ce<sup>3+</sup> was a strong nitrogen reduction site because Ce<sup>3+</sup> is in a more electron-rich state than is Ce<sup>4+</sup>.

From our study of the Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub> catalyst, we formulated a guiding principle for catalyst preparation, which is that reduction at high temperature induces the dynamics of the support and produces an active site at the interface with Ru. Following this guiding principle, we prepared a barium (Ba)-doped La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub> support, loaded it with Ru, and subjected it to high-temperature reduction, which afforded a Ru/Ba/LaCeO<sub>x</sub> catalyst with world-class ammonia synthesis performance.<sup>[5]</sup> We then subjected the reduced catalyst to TEM analysis (Figure 3). We found that the majority of the surface of the Ru nanoparticle was covered with nanosized oxides of low crystallinity (nanofractions) (Figure 3a) and that these nanofractions contained Ba, La, Ce<sup>4+</sup>, and Ce<sup>+3</sup> (Figure 3b). These elements have strong electron-donating ability; therefore, the Ru atoms adjacent to the nanofractions showed strong ability to donate electrons to nitrogen and high activity for nitrogen reduction. In addition, Ba was found to play a major role in the formation of these unique structures. The surface of the support is destabilized during the high-temperature reduction by forming a composite oxide incorporating Ba<sup>2+</sup> with a large ionic radius. To reduce their own surface energy, the resulting composite oxides migrate to the surface of the Ru nanoparticles as nanofractions. Like Ce<sup>3+</sup>, Ba is also extremely sensitive to atmospheric oxygen and water vapor; therefore, our non-air-exposure sample-loading technique proved useful for clarifying the structure and formation of the active site.

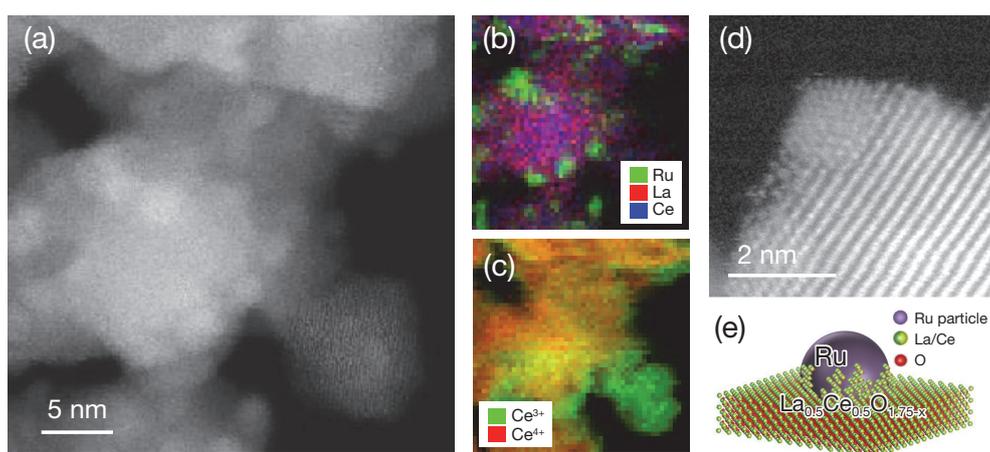


Figure 2 Microscopic analysis of Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub> without exposure to air. (a) High-angle annular dark-field (HAADF) image. (b) Elemental map of the catalyst, as determined by energy-dispersive X-ray fluorescence analysis. (c) Color map of the valence state of Ce, as determined by electron energy loss spectroscopy. (d) Atomic-resolution HAADF image of an Ru nanoparticle. (e) Schematic illustration of the Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub> surface after reduction.

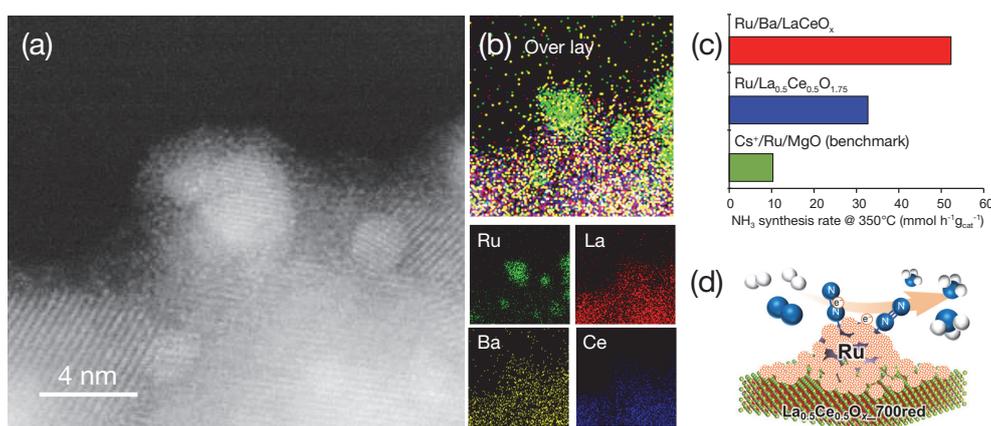


Figure 3 Microscopic analysis of Ru/Ba/LaCeO<sub>x</sub> without exposure to air. (a) Atomic-resolution high-angle annular dark-field image of the area around several Ru nanoparticles. (b) Elemental map of the catalyst, as determined by energy-dispersive X-ray fluorescence analysis. (c) Ammonia synthesis activity of Ru/Ba/LaCeO<sub>x</sub>, Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub>, and Cs<sup>+</sup>/Ru/MgO (benchmark). Reaction conditions: 1.0 MPa, SV = 72,000 mL h<sup>-1</sup> gcat<sup>-1</sup>, N<sub>2</sub>/H<sub>2</sub> = 1/3. (d) Schematic illustration of the active site of Ru/Ba/LaCeO<sub>x</sub> after reduction.

### Example application: Supported non-noble metal (Co) catalysts

We next extended our investigation to supported non-noble metal catalysts and found that Co@BaO/MgO, with magnesium oxide (MgO) as the support, exhibited very good ammonia synthesis activity.<sup>[6]</sup> Co@BaO/MgO not only achieved higher activity than conventional Co catalysts (250 times higher reaction rate per active site), but also surpassed that of an Ru-based benchmark catalyst (Figure 4). Elemental mapping revealed that the catalyst surface contained a structure comprising Co nanoparticles covered by nanofractions of BaO (Figure 4a). Results of

first-principles calculations suggest that formation of this structure promotes dissociation of adsorbed nitrogen as a result of most of the Co nanoparticle surface's becoming electron-rich from electron donation by BaO. Further microscopic analyses revealed the mechanism underlying the formation of the active sites: During high-temperature reduction, Ba species with low melting points are generated and dispersed over the support; Co nanoparticles then collect the Ba species as they are moved across the support by thermal vibrations, resulting in deposition of a BaO nanofraction on the surface of the Co nanoparticles.

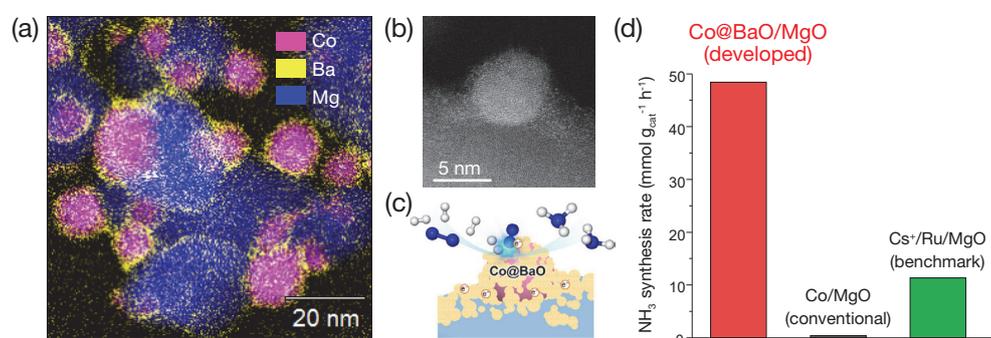


Figure 4 Microscopic analysis of Co@BaO/MgO. (a) Elemental map of the catalyst without exposure to air, as determined by energy-dispersive X-ray fluorescence analysis. (b) Atomic-resolution high-angle annular dark-field image of the area around several Co nanoparticles. (c) Schematic illustration of the surface of Co@BaO/MgO after reduction. (d) Ammonia synthesis activity of Co@BaO/MgO, Co/MgO, and Cs<sup>+</sup>/Ru/MgO. Reaction condition: 1.0 MPa, SV = 72,000 mL h<sup>-1</sup> gcat<sup>-1</sup>, N<sub>2</sub>/H<sub>2</sub> = 1/3, 350°C.

## Conclusion

Precise design of active sites is important for the development of highly active catalysts. Using our non-air-exposure analysis technique, we successfully developed several highly active catalysts for ammonia synthesis. We expect that our analysis technique will contribute to elucidating further guiding principles for the design of active sites, and to the realization of highly active catalysts for a broad range of reactions.

## References

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