

New Reaction Path in Ammonia Formation on Rh(111) Surface

Masanari NAGASAKA, Hiroshi KONDOH, Kenta AMEMIYA, Ikuyo NAKAI,
Toru SHIMADA, Reona YOKOTA, and Toshiaki OHTA*
Department of Chemistry, Graduate School of Science, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Introduction

Rhodium is mainly used as a three-way catalyst to convert nitrogen oxides from automotive exhausts to harmless nitrogen. Although the key step to promote the catalytic reaction is the dissociation of NO and the formation of N₂ gas, the ammonia formation from N and H is also important to understand the mechanism of the rhodium catalyst. Moreover, ammonia formation is the prototypical reaction for the sequential hydrogenation. For the ammonia formation, the N-preadsorbed Rh(111) is exposed to gaseous hydrogen at room temperature. In the past, it was believed that the reaction is the simple hydrogenation reaction: N + 2 H → NH₂ and NH₂ + H → NH₃↑ [1]. However, our time-resolved NEXAFS experiments observed a reverse reaction from NH₂ to form N and 2 H. The mechanism of ammonia formation on Rh(111) is so complicated that theoretical simulation is necessary for full understanding.

Experimental

The experiments were performed at BL-7A under ultrahigh vacuum condition (2.0×10^{-10} Torr). Time-resolved NEXAFS is a method to measure a NEXAFS spectrum in several seconds [2].

The atomic nitrogen covered Rh(111) surface was first prepared by exposing to 1.5 L gaseous NO at 150 K, annealing at 400 K to form N and O from the dissociation of NO, and exposing to 1.4 L gaseous H₂ at 400 K to remove O atoms. For the ammonia formation, the surface was exposed to gaseous H₂ (1.0×10^{-7} Torr) at 350 K. Each N-K NEXAFS spectrum was taken in 10 sec during H₂ exposure to monitor the real-time changes in N and NH₂ coverages. Note that the amount of NH₃ was obtained from the total coverage of N and NH₂ because NH₃ is immediately desorbed in this temperature region.

Results and Discussion

Figure 1 shows a time evolution of N K-NEXAFS spectra. As increasing exposure time, the peak due to atomic N (399.3 eV) disappears. The feature derived from NH₂ (408.0 eV) first increased and decreased later. After the reaction, no adsorbates remained on the surface. To obtain the coverage of each species, the spectra were fitted by the standard spectra of N and NH₂. Figure 2 shows the real-time change of N, NH₂, and NH₃ during the reaction. The NH₃ curve means the total desorbed NH₃ species. The obtained changes make us gain an insight into the reaction mechanism. At first, the N coverage

rapidly decreases and NH₂ grows until the ratio of N and NH₂ becomes constant. After reaching the equilibrium, both N and NH₂ coverages decrease gradually to form NH₃ gas.

When the H₂ gas was stopped during the reaction, the peak due to N rapidly increased, while the structure due to NH₂ decreases. It clearly suggests that the new reaction path, NH₂ → N + 2 H, is opened. That is why the reaction has the equilibrium due to this reverse reaction.

To interpret the experimental results and to understand the reaction mechanism in more detail, atomic-level kinetic simulation should be necessary. DFT-Monte Carlo simulations for this reaction are now underway.

References

- [1] R. M. van Hardeveld et al., *J. Phys. Chem. B* 101, 998 (1997).
- [2] K. Amemiya et al., *Jpn. J. Appl. Phys.* 40, L718 (2001).

* ohta@chem.s.u-tokyo.ac.jp

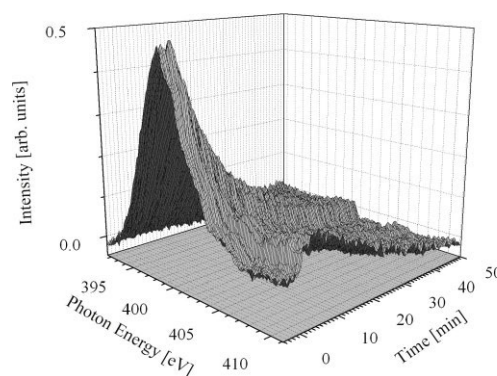


FIG. 1. N-K NEXAFS spectra at grazing incidence as a function of time (350 K, H₂: 1.0×10^{-7} Torr).

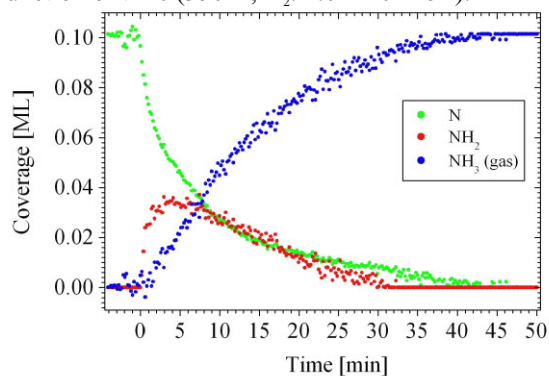


FIG. 2. Coverages of N, NH₂, and NH₃ as a function of time obtained from Fig. 1. The NH₃ desorbs from the surface.