

Mechanism of N+NO reaction on Rh(111) surface studied with energy-dispersive NEXAFS

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Introduction

Catalytic reduction of NO into molecular nitrogen on rhodium surfaces in the presence of CO is widely used to control air pollution. The most important step in the total reaction is the conversion of atomic N into molecular N₂, but its mechanism is not clear yet. As the N-O bond scission occurs above 400 K, most of the previous study of the reaction mechanism was conducted at high temperatures [1]. We prepared atomic-N covered Rh(111) surfaces and studied the reactivity with NO to understand the mechanism of the N+NO reaction at low temperatures.

Experimental

The experiments were carried out at BL-7A with an UHV system. First, an atomic-nitrogen overlayer was prepared on a clean Rh(111) surface; molecularly adsorbed NO was dissociated at 400 K, and generate atomic oxygen was removed by the reaction with H₂. Then the N-covered Rh(111) surface was exposed to gaseous NO of a constant pressure at a constant surface temperature. The clean-off process of N with NO was monitored with N K-edge energy-dispersive NEXAFS, with which a NEXAFS spectrum is obtained in several seconds [2]. From the obtained series of spectra, the time evolution of coverages of N and NO was extracted by curve-fitting analysis.

Results and discussion

A typical result is shown in Fig. 1. An induction period precedes the reaction. The reaction rate was estimated from the slope of the reduction of N, and its temperature dependence was plotted in Fig. 2. The temperature dependence is classified into three regions.

The most interesting is that in the region II, the reaction rate decreases with increasing reaction temperature, which is contrary to the case of usual thermally activated reactions. This indicates that a weakly bound adspecies in equilibrium with the gas-phase NO is involved in the reaction as a precursor. In this region, the total reaction is expressed as $N+NO \rightarrow N_2O \uparrow$, but the chemisorbed NO molecules bound to the Rh substrate do not directly react with N atoms.

In the region I, the reaction rate decreases as the surface temperature decreases. The consumption of the precursor by the reaction becomes slower than its accumulation due to the low temperature. In this region, NO dimer, (NO)₂ formed above an NO chemisorption layer was observed during the reaction. The observed NO dimer in the second layer corresponds to the precursor suggested in the region II. It easily reacts with atomic N bound to the Rh surface to form N₂O below 370 K.

In the region III, a completely different reaction occurs. Two possible paths are proposed; chemisorbed NO reacts with N and generated N₂O immediately dissociates into N₂ and O ($NO_a+N_a \rightarrow N_2O_a \rightarrow N_2 \uparrow + O_a$), or a 'hot' N atom formed by the dissociation of NO reacts with an adsorbed N atom ($NO_a+N_a \rightarrow N_2 \uparrow + O_a$).

References

- [1] F. Zaera *et al.*, *Chem. Phys. Lett.* **332**, 209 (2000), *etc.*
- [2] K. Amemiya *et al.*, *Jpn. J. Appl. Phys.* **40**, L718 (2001).

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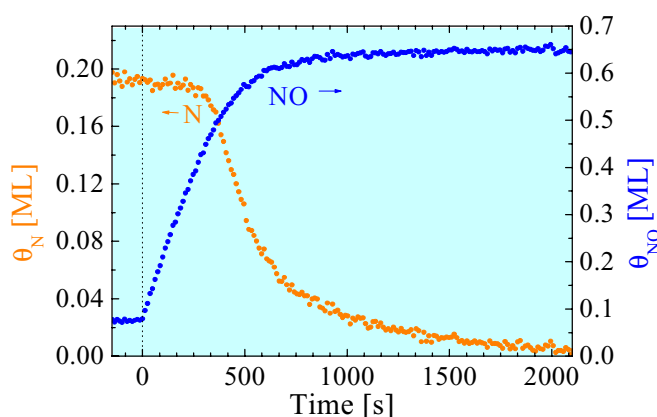


Fig. 1: Time evolution of the coverages of N and NO during the N+NO reaction at 120 K ($P_{NO}=5 \times 10^{-9}$ Torr)

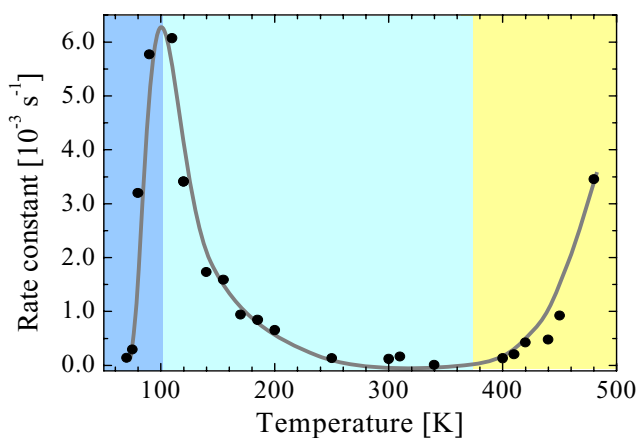


Fig. 2: Temperature dependence of the reaction rate at the initial stage of the N+NO reaction. ($P_{NO}=5 \times 10^{-9}$ Torr)