AR-NW10A/2024G060

Monitoring of Ru Site Temperature for Photocatalytic Ammonia Synthesis

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1 Introduction

Ammonia production requires large amounts of equipment and energy. In addition to its traditional use as a fertilizer, ammonia is finding new roles as a transport medium to produce hydrogen and electricity. Considering the increasing demand of ammonia, improving the energy efficiency of ammonia production has significant implications for the global environment. Herein, an EXAFS analysis of the photocatalytic synthesis pathway from N_2 to NH_3 is reported using a Ru–CeO_2 catalyst.

In this report, the valence state, site structure, and temperature of the Ru sites were monitored under N_2, H_2, and UV–visible light irradiation.

2 Experiments

Ru–CeO_2 photocatalyst was prepared via impregnation method from Ru(III) nitrosyl nitrate and CeO_2 by mixing, evaporating the water, and heated at 673 K under hydrogen.

Ru K-edge XAFS spectra were measured in the transmission mode at the Photon Factory Advanced Ring, High Energy Accelerator Research Organization on the NW10A beamline equipped with a Si (3 1 1) monochromator, a Pt-coated mirror, and a piezo transducer.

The obtained Ru K-edge XAFS data were analyzed using the XDAP software package version 3.2.9 [1]. Multiple-shell curve-fit analyses were performed with the data using the theoretical amplitude and phase shift functions calculated using a multiple scattering calculation code FEFF version 8.4 [2].

3 Results and Discussion

When the photoreaction was carried out using a catalyst in a quartz reaction cell in a flow system with a nitrogen/hydrogen ratio of 1: 3, ammonia was formed at a rate of 132.4 μmol h^{-1} g_{cat}^{-1}.

In the Fourier transform of the angular wave number k^3-weighted Ru K-edge EXAFS χ-function for the most active Ru–CeO_2 photocatalyst, two peaks appeared at 0.18 and 0.24 nm owing to Ru–O and Ru–Ru pairs, respectively (Figure 1). The curve fit to the latter peak provided fit parameters of interatomic distance 0.2624 nm, coordination number 2.6, and Debye–Waller factor σ^2 8.75 × 10^{-5} nm^2,

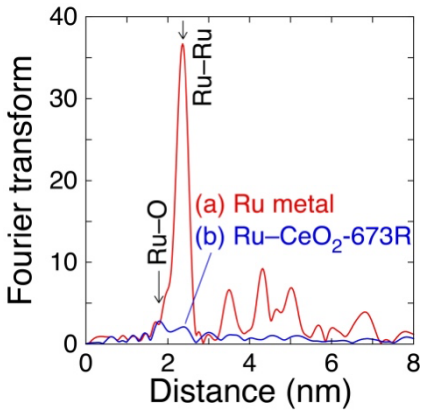

Figure 1. Fourier transform of angular wavenumber k^3-weighted Ru K-edge EXAFS χ-function measured for (a) Ru metal and (b) Ru (2.5 wt %)–CeO_2 heated at 673 K under H_2.

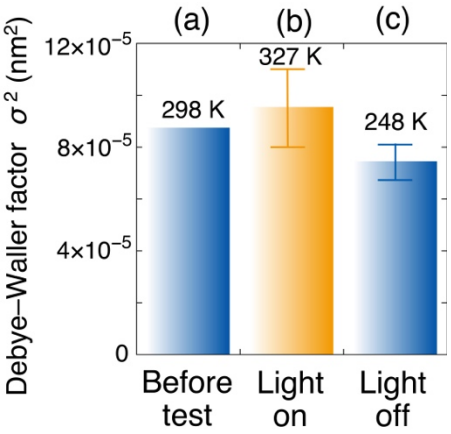

Figure 2. The changes of Debye–Waller factor for Ru site in Ru–CeO_2 photocatalyst under H_2 and N_2 (a) before and (b) during UV–visible light irradiation and (c) after UV–visible light was turned off.

indicating the number of Ru atoms constituting a particle was 3–4. Figure 2 shows the result of temperature monitoring of Ru based on theoretical correlation between the temperature of a particle consisting of three Ru atoms and the Debye-Waller factor calculated using FEFF with the surface Debye temperature value for Ru (295 K) [3].

The temperature of Ru sites at 298 K before UV–visible light irradiation increased to 327 ± 50 K under N_2, H_2, and UV–visible light irradiation for 112 min (Figure 2(b)). When the light was turned off, the

temperature decreased quickly to 248 ± 20 K (Figure 2(c)).

References

[1] Vaarkamp, M.; Linders, H.; Koningsberger, D. XDAP Version 3.2.9.; XAFS Services International: Woudenberg, The Netherlands, 2022.

[2] Ankudinov, L.; Ravel, B.; Rehr, J. J.; Condradson, S. D. *Phys. Rev. B* **1998**, *58*, 7565–7576.

[3] Ferrari, E.; Galli, L.; Miniussi, E.; Morri, M.; Panighel, M.; Ricci, M.; Lacovig, P.: Lizzit, S.; Baraldi, A. *Phys. Rev. B* **2010**, *82*, 195420.

Research Achievements

1. 渡辺裕太、佐々木将人、能島昭史、牧野伸彦、久 正明、中嶋孝宏、泉 康雄、Ru 数原子粒子担持 CeO_2 を使用した光触媒的アンモニア合成、日本化学会第 105 春季年会、C403-2am-15、2025 年 3 月 26〜29 日（発表日 3 月 27 日）、吹田市.

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