

μ -XAFS analysis of a single catalyst particle of $\text{NiO}_x/\text{Ce}_2\text{Zr}_2\text{O}_y$ on a SiO_2 membrane using X-ray μ -beam

Various heterogeneous catalysts have been used in chemical industry processes, such as oil and natural gas conversions, energy conversions, and the synthesis of fundamental chemical compounds. Solid catalysts are usually inhomogeneous powder assemblies of heterogeneous solid particles with nm– μm size, and each powder particle has different shape and structure. Therefore, the structures of solid catalysts are often complex and difficult to characterize by a simple method.

Synchrotron XAFS is one of the most powerful methods for characterizing oxidation states and local coordination structures of heterogeneous solid catalysts, such as supported metal catalysts. However, conventional XAFS measurements are performed using X-ray beams with mm size and they provide macroscopically averaged structural information on a large number of heterogeneous catalyst particles with different sizes, compositions, and local coordination structures in beam-spot size.

We have succeeded in performing the scanning μ -XRF and μ -XAFS analyses of a single catalyst particle of $\text{NiO}_x/\text{Ce}_2\text{Zr}_2\text{O}_y$ ($0 \leq x \leq 1$, $7 \leq y \leq 8$) using an X-ray μ -beam (1000 nm (h) \times 800 nm (v)) at beamline **BL37XU**. $\text{Ce}_2\text{Zr}_2\text{O}_y$ solid solution is known to exhibit a high oxygen storage/release property, which is highly important for automobile exhausting catalysts [1]. Its oxygen composition can be controlled between $\text{Ce}_2\text{Zr}_2\text{O}_7$ and $\text{Ce}_2\text{Zr}_2\text{O}_8$, and the Ni species supported on $\text{Ce}_2\text{Zr}_2\text{O}_7$ is active for CH_4 steam reforming reaction ($\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}$) to produce hydrogen [2]. Its activity highly depends on the oxidation state and local coordination structure of the Ni species supported on $\text{Ce}_2\text{Zr}_2\text{O}_y$. The average particle size of the $\text{NiO}_x/\text{Ce}_2\text{Zr}_2\text{O}_y$ catalyst was 750 ± 370 nm, which is similar to the size of the X-ray μ -beam. The scanning μ -XRF and μ -XAFS analyses of a single catalyst

particle of $\text{NiO}_x/\text{Ce}_2\text{Zr}_2\text{O}_y$ revealed the microscopic structural information (oxidation state and local coordination structure) of catalytically active and inactive phases of a single particle of the supported Ni catalyst for CH_4 steam reforming reaction for the first time [3].

Figure 1(a) shows the experimental setup used for the μ -XRF and fluorescent μ -XAFS analyses at BL37XU. The X-ray beam was focused by Kirkpatrick-Baez (KB) mirrors and the size of the obtained X-ray μ -beam was 1000 nm (h) \times 800 nm (v) at the Ni K-edge (8.332 keV) (Fig. 1(b)). The $\text{NiO}_x/\text{Ce}_2\text{Zr}_2\text{O}_y$ catalyst particles were dispersed on a thin SiO_2 membrane (30 μm), and the membrane in a XAFS cell was mounted on a piezoelectric translation stage at the focusing point of the X-ray μ -beam. The fractions of aggregated particles on the membranes were estimated to be less than 1.9% by the analysis of SEM images. We prepared $\text{Ni}/\text{Ce}_2\text{Zr}_2\text{O}_7$ and $\text{NiO}/\text{Ce}_2\text{Zr}_2\text{O}_8$ dispersed on the SiO_2 membranes and recorded the results of the μ -XRF and fluorescent μ -XANES and μ -EXAFS analyses.

Two-dimensional (2D) scanning for μ -XRF mapping was performed using the X-ray μ -beam at 8.248 keV, and Ni K α (7.478 keV) and Ce L α (4.840 keV) + L β_1 (5.262 keV) fluorescent X-rays were measured. The piezoelectronic stage was shifted every 200 nm and 2D μ -XRF images of the fluorescent X-ray intensity were obtained. In the case of a conventional XAFS measurement using an mm-sized X-ray beam, the observed XAFS data involves contribution from all catalyst particles in the beam spot, but the μ -XAFS data provides the structural information of a single catalyst particle in the μ -beam spot, as illustrated in Fig. 2(a). Similar contrast images were observed for Ni K α and Ce L α + L β_1 fluorescent X-rays, indicating the

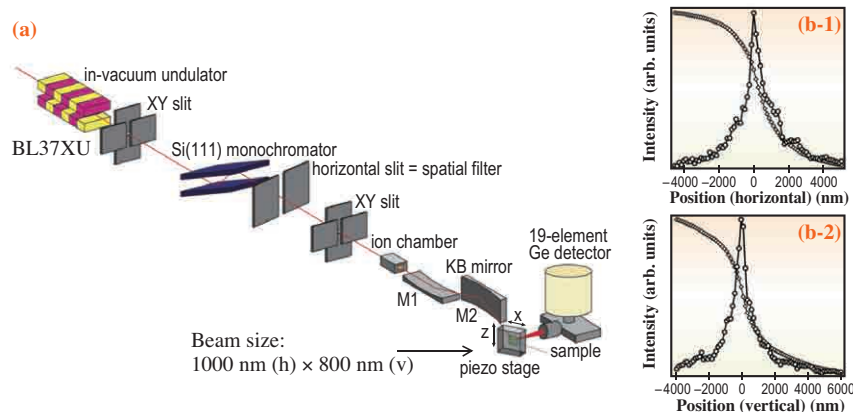


Fig. 1. (a) Experimental setup of μ -XAFS. (b) Measured knife-edge profiles of focused X-ray μ -beam at 8 keV. (b-1) Horizontal direction and (b-2) vertical direction.

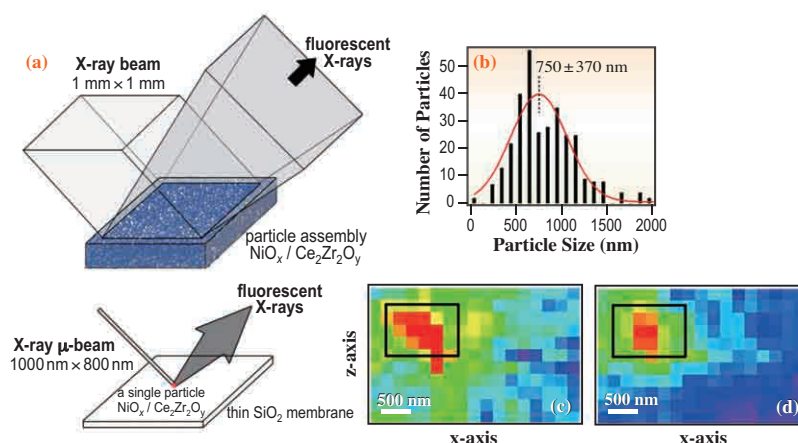


Fig. 2. (a) Schematic of conventional XAFS and μ -XAFS measurements. (b) Particle size distribution of the NiO_x/Ce₂Zr₂O_y catalyst. (c) and (d) 2D μ -XRF mappings of a NiO/Ce₂Zr₂O₈ particle on a SiO₂ membrane ((c): Ni K α and (d): Ce L α +L β ₁).

position of the catalyst particle on the SiO₂ membrane (Figs. 2(b) and 2(c)).

Significant differences in Ni *K*-edge XANES were observed for Ni/Ce₂Zr₂O₇, which is active for CH₄ steam reforming reaction and NiO/Ce₂Zr₂O₈, which is inactive for the reaction, as shown in Fig. 3(a). The μ -XANES spectra of Ni/Ce₂Zr₂O₇ (i) and NiO/Ce₂Zr₂O₈ (iii) were similar to the XANES spectra of the Ni/Ce₂Zr₂O₇ particle assembly (ii) and NiO/Ce₂Zr₂O₈ particle assembly (iv), respectively. The Ni *K*-edge energies of μ -XANES were 8.338 and 8.341 keV for Ni/Ce₂Zr₂O₇ (i) and NiO/Ce₂Zr₂O₈ (iii), respectively, reflecting the oxidation state of the supported Ni species on Ce₂Zr₂O_y. Although the white line intensity of μ -XANES of the active Ni/Ce₂Zr₂O₇ catalyst (i) was slightly higher than that of conventional XANES (ii) owing to the probable oxidation with impurity oxygen under the measurement conditions, these results show that the oxidation state of the single catalyst particle can be discriminated by μ -XANES analysis. Intermediate oxidation states between NiO_x/Ce₂Zr₂O_y samples ($7 < y < 8$).

We have succeeded in analyzing a Ni *K*-edge μ -EXAFS spectrum of a single catalyst particle of the inactive NiO/Ce₂Zr₂O₈ (Figs. 3(b)–3(d)). The EXAFS spectrum was measured for 3 h and its *k*³-weighted EXAFS oscillations and Fourier transforms were successfully fitted. The obtained structural parameters of the local coordination of Ni species on the NiO/Ce₂Zr₂O₈ catalyst particle showed that the Ni species was NiO(II) (CN of Ni-O (at 0.208 ± 0.003 nm) = 5.4 ± 1.2; CN of Ni-Ni (at 0.292 ± 0.001 nm) = 11.7 ± 0.9). To our knowledge, this was the first example of the μ -EXAFS curve-fitting analysis of a single catalyst particle of a practical catalyst. μ -XAFS will provide structural information regarding the catalyst particles with different catalytic behaviors excluding noise information from the heterogeneous property of

catalyst particle assembly and contribute to the development of a more precise catalyst design in chemical reactors.

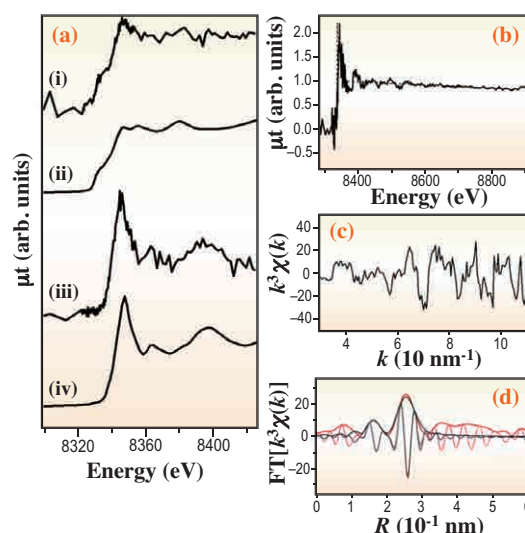


Fig. 3. (a) Ni *K*-edge XANES spectra of Ni/Ce₂Zr₂O₇ (i: μ -XANES of a single particle on a SiO₂ membrane and ii: conventional XANES of particle assembly) and NiO/Ce₂Zr₂O₈ (iii: μ -XANES of a single particle on a SiO₂ membrane and iv: conventional XANES of particle assembly). (b) μ -EXAFS data of NiO/Ce₂Zr₂O₈, (c) its *k*³-weighted EXAFS oscillation, and (d) its Fourier transforms.

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