Efficient and Selective Interplay of Ni and ZrO, for CO, Photoconversion into CH₄ Revealed by Extended X-Ray Absorption **Fine Structure Debve–Waller Factor**

An efficient photocatalyst comprising Ni nanoparticles and ZrO₂ has been found to photoconvert CO₂ into CH₄, and the interplay of Ni and ZrO₂ was investigated by Ni and Zr K-edge extended X-ray absorption fine structure (EXAFS) Debye-Waller factor. Based on the correlated Debye model, the Ni site temperature reached 394 K irradiated under UV-visible light by the transformation of absorbed light energy into heat. As a result, CO (or formate species) was converted into CH₄ over the Ni surface while the UV light excited electrons at the valence band of ZrO₂ to the conduction band, leading to the reduction of CO_2 to CO.

Photocatalytic conversion of CO₂ into fuels completes the carbon-neutral cycle in a sustainable society utilizing renewable light energy. To investigate efficient and selective photocatalysts for the conversion, it is essential to understand the reaction mechanism. The Ni–ZrO₂ photocatalyst formed CH₄ at a rate of 0.98 mmol $h^{-1} g_{cat}^{-1}$ from CO₂ [1]. The study investigated the catalytic role of Ni by Ni K-edge EXAFS based on the correlated Debye model [2, 3].

The Fourier transform showed a typical pattern for metallic Ni sites before light irradiation [Fig. 1(A)]. The

major peak intensity at 0.21 nm quickly decreased to 78% within 20 min of irradiation and essentially remained the same for 130 min. The time-course changes of the major fit parameters, coordination number N and Debye–Waller factor σ , for the Ni–Ni interatomic pair are illustrated in Fig. 1(C) and (D), respectively.

The σ value was calculated as 0.00492 nm for Ni metal at 295 K based on the correlated Debye model using ab initio multiple-scattering calculation code FEFF8.4 [4] and the Debye temperature of Ni [450 K; Fig. 1(E)-(a)]. The XDAP code [5] provided



Figure 1: Ni K-edge EXAFS for Ni-ZrO2 under CO2 and H2. (A, B) Time-course change in Fourier transform of angular wavenumber k^3 -weighted EXAFS χ function irradiated by UV-visible light (A) and under dark (B). (C, D) Coordination number N (C) and Debye–Waller factor σ (D) of the Ni–Ni shell. (E) Theoretical temperature dependence of σ of the bulk site (a) and surface site for vertical and horizontal motions to the surface (b, c).

UV (C) HO

Scheme 1: Proposed photocatalytic reaction mechanism of CO2 reduction to CH4

the experimental difference for the σ^2 value from that of the Ni metal (model). Furthermore, we consider that the contribution of structural disorder [6] for the σ value is the difference of the σ value from the Ni metal.

 $\sigma^2 = \sigma_{\text{correlated Debve}}^2 + \Delta(\sigma_{\text{structural disorder}}^2) + \Delta(\sigma_{\text{XDAP}}^2)$

To adjust the theoretical temperature estimated for the Ni-ZrO₂ sample measured at 295 K, the $\sigma_{
m structural \, disorder}$ value was evaluated as 0.00313 nm.

Apparently, the N(Ni-Ni) value negligibly changed within 8.3±0.2 [Fig. 1(C)] during light irradiation, whereas the σ (Ni–Ni) value guickly increased from 0.00585 nm before irradiation to 0.00745 nm within 20 min of irradiation, and remained at 0.00751±0.00008 nm [Fig. 1(D)].

Then, the UV-visible light was turned off and the σ (Ni–Ni) value quickly decreased to 0.00587 nm within 10 min and negligibly changed while the N(Ni-Ni) value still remained approximately the same, at 8.4±0.2 for 111 min.

We evaluated the temperature at Ni sites based on σ values. The temperature dependence of σ values is plotted in Fig. 1(E). The different dependence for the motion of vertical and horizontal freedom of translation at the surface Ni atom is due to different Debye temperatures of 208 K and 348 K, respectively, in comparison to bulk Ni (450 K). We approximated the mean Ni nanoparticle temperature as the arithmetic mean value based on each temperature dependence as shown in Fig. 1(E) for mean 1.7 nm Ni particles.

Thus, the initial temperature of Ni sites (295 K) guickly increased to 389 K within 20 min after the UV-visible light irradiation began and remained essentially constant (389–394 K) during light irradiation. When the UV-visible light was turned off, the temperature suddenly decreased to 296 K within 10 min [Fig. 1(D)].

Based on the heat capacity of Ni and ZrO₂ and tem-



perature trend [Fig. 1(D)], the origin of the temperature change was exclusively light energy converted in Ni. The reaction step from CO (or formate species) to CH₄ proceeded on the heated Ni surface [Scheme 1(d)-(f)] combined with the first part of the catalysis over ZrO_2 : CO_2 to CO owing to charge separation by light [Scheme 1(a)-(d)].

The σ values for Zr K-edge EXAFS for Ni–ZrO₂ did not change significantly under irradiation of UV-visible light, indicating that mean 1.7 nm Ni was heated as the dynamic equilibrium between absorbed light energy conversion and guick heat dissipation to ZrO₂ and quartz/Pyrex glass reactor. This temperature monitoring technique has also been applied to growing metal nanoparticles from 0.5 to 3.6 nm and to evaluating enthalpy changes of chemical reactions [7].

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BEAMLINES

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