

XAFS study for Zn doped in gallium oxide photocatalyst

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Nagoya 464-8603, Japan**Introduction**

Ga₂O₃ photocatalysts showed a high and stable activity for the photocatalytic steam reforming of methane (PSRM; $2\text{H}_2\text{O}_{(g)} + \text{CH}_4 \rightarrow 4\text{H}_2 + \text{CO}_2$) around room temperature [1]. The activity was much influenced by not only the cocatalyst and the crystal structure of Ga₂O₃ but also the addition of metal cations into the bulk and/or on the surface of Ga₂O₃. Metal cation having both a smaller oxidation number than that of Ga³⁺ and a similar ionic radius to that of Ga³⁺, such as Zn²⁺, was effective as the dopant into the bulk of β-Ga₂O₃. In this study, we investigated the local structure of Zn ions doped in Ga₂O₃ by using XAFS spectroscopy.

Experimental

The Zn precursor was Zn(NO₃)₂·6H₂O (Kishida, 99.0%). β-Ga₂O₃ (2 g, Kojundo) was dispersed into an aqueous solution (50 ml) of the Zn(NO₃)₂ and stirred for 0.5 h before evaporation to dryness, followed by drying in an oven at 333 K overnight and calcination in air at 773–1473 K for 6 h to obtain Zn-doped Ga₂O₃ samples. On the other hand, ZnGa₂O₄ was prepared by a solid-state reaction method at 1473 K.

Zn K-edge XAFS spectra were recorded at the NW-10A station [2] of KEK-PF at room temperature with a Si(311) double crystal monochromator in a transmission mode. The samples were packed in each polyethylene film cell in air. The spectra were analyzed with a REX 2000 software (Rigaku).

Results and discussion

Fig. 1A shows Zn K-edge XANES spectra of the samples. The spectrum of the Zn-loaded Ga₂O₃ sample calcined at 773 K was almost the same as that of the ZnO sample. When the calcination temperature increased to 1073 K and higher temperatures, the spectrum became almost the same as that of the ZnGa₂O₄ spinel. These results suggest that the Zn ions would exist in the ZnO particles when the calcination temperature was 773 K, on the other hand, Zn ions in the sample calcined at 1073 K and higher temperatures would have a local structure like as the ZnGa₂O₄ spinel. Fig. 1B shows the Fourier transforms of Zn K-edge EXAFS spectra for these samples. The first coordination peak assignable to the Zn–O shell around 1.2–1.9 Å could not be available for the detailed analysis due to the similar atomic distances for the Zn–O both in the ZnO (1.98 Å) and ZnGa₂O₄ (1.98 Å) and the Ga–O in the β-Ga₂O₃ sample (1.8–2.0 Å). However, the second coordination sphere assignable to

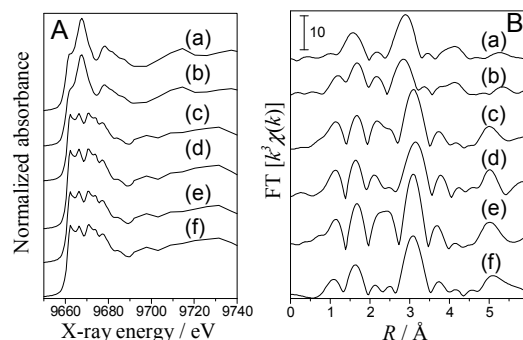


Fig. 1 (A) XANES and (B) Fourier transforms of Zn K-edge EXAFS spectra for (a) ZnO, (b)–(e) the Zn(2 mol%)-loaded β-Ga₂O₃ samples and (f) ZnGa₂O₄. Calcination temperature was (b) 773 K, (c) 1073 K, (d) 1273 K and (e) 1473 K.

the Zn–metal shell around 2.5–3.5 Å provided clear evidences through the curve fitting analysis with the empirical parameters extracted from the second coordination peak for the Zn–Zn and Zn–Ga shells in the spectra of the ZnO and ZnGa₂O₄ samples, respectively. The second coordination peak for the Zn-loaded β-Ga₂O₃ calcined at 773 K was only composed of the Zn–Zn shell with almost the same length as that in the ZnO sample (3.22 Å). On the other hand, for the sample calcined at 1073 K and higher temperatures, it was only composed of the Zn–Ga shell with the same length as that in the ZnGa₂O₄ sample (3.46 Å).

Thus, it is concluded that the Zn ions would be existed as ZnO metal oxide species on the Ga₂O₃ surface without mixing with the Ga₂O₃ when calcined at 773 K, and when calcined at 1073 K and higher temperatures, they would react with the Ga₂O₃ to form the spinel ZnGa₂O₄ partially or substitute Ga ion in the β-Ga₂O₃ having a spinel-like local structure. Since the band gap of ZnGa₂O₄ (4.3 eV) [3] was a little smaller than that of β-Ga₂O₃ (4.7 eV), the small ZnGa₂O₄ composites on the surface layer of the β-Ga₂O₃ photocatalysts might promote the separation of photoexcited carriers to enhance the photocatalytic activity. The influence of the dopant on the electron density would be also considered as another possibility.

References

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