

## Photocatalytic Active Sites of Silica-supported Gallium Oxide for Non-oxidative Direct Methane Coupling

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### Introduction

Gallium oxide, in which gallium can be found as tetrahedral and/or octahedral coordination states, has been reported to be important for many catalytic reactions, such as reduction of NO and alkane dehydrogenation.<sup>1,2</sup> It was found that the local structure of gallium oxide affected the catalytic activity for NO reduction.<sup>1</sup>

On the other hand, XANES spectroscopy has been proposed to be a good method to analyze the coordination states of gallium oxides quantitatively.<sup>3</sup> In the present study, a series of silica-supported gallium oxide samples were tested for photocatalytic non-oxidative direct methane coupling and Ga K-edge XANES spectroscopy was carried out in order to reveal the local structure of photoactive sites in the samples.

### Experimental

As support we used amorphous silica that was prepared by sol-gel method, followed by calcining at 773 K for 5 h, with specific surface area was 554 m<sup>2</sup>g<sup>-1</sup>. Silica-supported gallium oxide samples, Ga/SiO<sub>2</sub>(*x*), were prepared by impregnation of the silica support with an aqueous solution of gallium nitrate, drying at 383 K in an oven overnight and calcination at 773 K for 5 h, where *x* showed mol% of Ga to total cation of Ga and Si. β-Ga<sub>2</sub>O<sub>3</sub> was commercially obtained and employed as a reference compound.

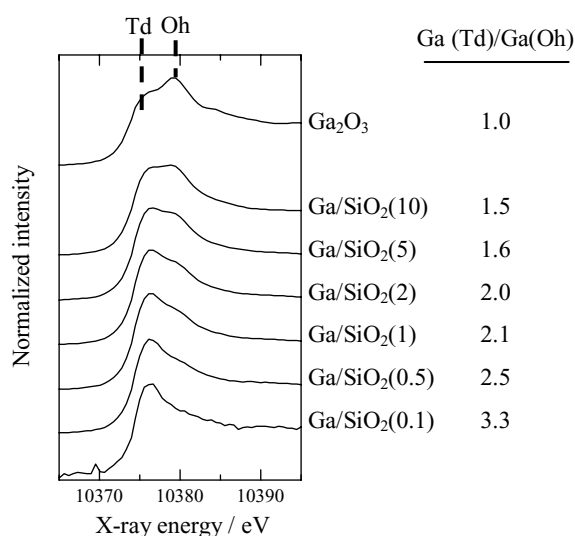
The Ga K-edge XANES measurement was performed at room temperature in transmission mode (*Ga* > 1 mol%) and fluorescence mode (*Ga* ≤ 1 mol%) at the BL-10B station of KEK-PF, Tsukuba, Japan, with a Si(311) channel-cut monochromator. Before recording XANES spectra, the sample was pretreated with 13.3 kPa of oxygen for 1 h at 1073 K, followed by evacuation for 1 h at 1073 K. Then the sample was sealed with a polyethylene film in a dry atmosphere. The photocatalytic test was carried out as in the previous study.<sup>4</sup> Before photoreaction, the samples were treated as the pretreatment before recording the XANES spectra.

### Results and discussion

For analysis of XANES spectra, β-Ga<sub>2</sub>O<sub>3</sub> was used as a reference, where the ratio of tetrahedral (Td) to octahedral (Oh) species was reported to be near to one.<sup>3</sup> Ga(Td) species exhibits an absorption peak at 10375.2 eV, while Ga(Oh) species exhibits an absorption peak at 10379.1 eV, as shown in Fig.1. The samples with low loading of Ga on silica support showed the dominant peak of Ga(Td),

suggesting the presence of Ga(Td) as the main species, while samples with high loading of Ga showed the presence of both Ga(Td) and Ga(Oh) species. The ratio of tetrahedral to octahedral species obtained by deconvolution using the curve-fitting method<sup>3</sup> is also shown for each sample in Fig. 1.

Photoreaction results showed that the silica-supported gallium oxides samples exhibited higher activity than



**Fig. 1** Normalized Ga K-edge XANES spectra of Ga/SiO<sub>2</sub> samples and Ga<sub>2</sub>O<sub>3</sub> as a reference compound. The Ga(Td)/Ga(Oh) for each sample is also shown.

silica support. The main product was ethane. It was confirmed that the hydrocarbons and hydrogen were produced almost stoichiometrically over samples with low loading of Ga. However, in the case of high loading samples, the amount of detected hydrogen was lower than the amount calculated from detected hydrocarbons. It seemed that the hydrogen would be consumed during the photoreaction. Thus, it is proposed that the highly dispersed Ga(Td) species is the photocatalytic active sites for non-oxidative direct methane coupling.

### References

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