

XAFS study of La ions doped in NaTaO₃ photocatalyst

Katsuya SHIMURA, Hisao YOSHIDA*

Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Introduction

The development of a hydrogen production method from renewable resources and natural energy would be important to realize a sustainable society. Photocatalytic steam reforming of methane ($\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{CO}_2$) is an attractive reaction because it has a potential to produce hydrogen from water and biomethane by using solar energy. We reported that Pt-loaded photocatalyst showed activity for this reaction at room temperature, among which Pt-loaded La-doped NaTaO₃ (NaTaO₃:La) showed the highest activity so far [1]. La-doping was also reported to increase the photocatalytic activity of NaTaO₃ for water decomposition [2]. In this study, we examined the local structure of La ions in NaTaO₃ with XAFS.

Experimental

NaTaO₃:La was prepared by solid-state reaction method [1, 2]. Pt co-catalyst was loaded by impregnation method. Photocatalytic reaction was carried out with a fixed-bed flow-type reactor.

La K-edge XAFS spectra were recorded at the NW-10A station at KEK-PF in a transmission mode for La₂O₃ and NaTaO₃:La(1-3%) samples and in a fluorescence mode for NaTaO₃:La(0.5-1%) samples. The spectra were analyzed with REX 2000 software (Rigaku). Fourier transform was performed in the range of ca. 5-12 Å⁻¹ after background subtraction. The inverse Fourier transform was carried out in the range of ca. 2.6-3.8 Å. The theoretical parameters were used for curve fitting analysis.

Result and Discussion

Fig. 1 shows the Fourier transforms of EXAFS spectra for La₂O₃ and NaTaO₃:La(0.5-3%) samples. For La₂O₃, the first peak around 2.1 Å corresponds to a La-O shell and the second coordination peak around 3.8 Å is assigned to a La-La shell. In the NaTaO₃:La samples, the region for the first coordination peak was complicated but the second coordination peak was clearly observed around 3.1 Å.

Table 1 shows the curve-fitting results of NaTaO₃:La

samples. It was revealed that the second coordination sphere of the doped samples was mostly composed of a La-Ta shell and there was also a La-La shell as a minor fraction. As the doping amount of La increased, the ratio of the La-La shell increased. The length of the La-Ta shell was almost the same as the atomic distance between Na and Ta in NaTaO₃ (3.27-3.45 Å) and the length of the La-La shell was almost the same as the atomic distance between Na and Na in NaTaO₃ (3.88 Å). These suggest that La ions substituting for the lattice Na⁺ in NaTaO₃ with a high dispersion would be major when the doping amount of La was small. However, the number of La ions substituting for the adjacent Na sites to form La-La pair in NaTaO₃ increased with further increasing the doping amount. Since the photocatalytic activity became the highest value on the 2%-doped sample, it was concluded that the former would increase the activity and the latter would decrease it.

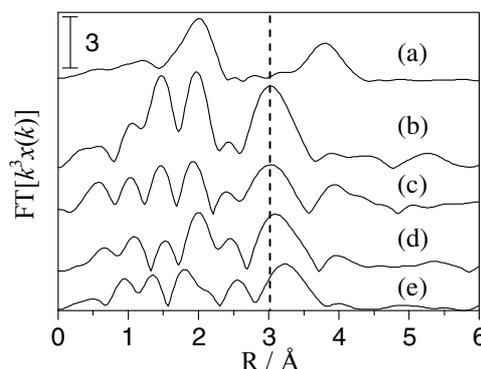


Fig. 1 Fourier transformed La K-edge EXAFS spectra of (a) La₂O₃ and (b)-(e) NaTaO₃:La(x%) samples; where x was (b) 0.5%, (c) 1%, (d) 2% and (e) 3%.

References

- [1] H. Yoshida, et al., *Chem. Lett.*, **36** 430 (2007).
 [2] H. Kato et al., *J. Am. Chem. Soc.*, **125**, 3082 (2003).

* yoshidah@apchem.nagoya-u.ac.jp

Table 1 Result of EXAFS analysis and the photocatalytic activity of NaTaO₃:La samples

Doping amount / mol%	La-Ta		La-La		H ₂ production rate ^c / μmol min ⁻¹
	N ^a	R ^b / Å	N ^a	R ^b / Å	
0.0	-	-	-	-	0.01
0.5	2.7	3.30	0.0	-	0.78
1.0	3.4	3.36	0.1	3.90	1.0
2.0	3.4	3.40	0.4	3.88	1.6
3.0	2.9	3.44	0.6	3.88	0.85

^a N: coordination number. ^bR: atomic distance. ^c In the photocatalytic steam reforming of methane over Pt(0.01 wt%)/NaTaO₃:La.