

XAFS Study of Indium Oxide Modified by Addition of Scandium

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1 Introduction

Recently, our group revealed that scandium-modified In_2O_3 catalyst was notably active for the direct conversion of ethanol to propene, and the propene yield reached approximately 60% at 30% partial pressure of ethanol [1]. It is important to note that the theoretical maximum yield of propene based on equation ($2\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_2=\text{CHCH}_3 + \text{CO}_2 + 3\text{H}_2$) was 75%, due to the side production of carbon dioxide, and therefore the 60% yield corresponded to 80% of the theoretical maximum value and was sufficiently high. In this study, the effect of scandium addition onto In_2O_3 was examined by using XAFS spectroscopy.

2 Experimental

Indium oxide was commercially obtained from Kanto Chemical Co. Japan. Scandium-loaded In_2O_3 sample was prepared by a conventional impregnation method using scandium acetate. The catalyst was designated as $\text{Sc3}/\text{In}_2\text{O}_3$, where "3" was the amount of loaded scandium (atomic % to that of In). In_2O_3 and $\text{Sc3}/\text{In}_2\text{O}_3$ samples were calcined at 1073 K for 5 h. In the XAFS experiments, the sample was pressed into a self-supporting disk with a diameter of 10 mm, placed in a quartz cell, and heated under flowing N_2 at elevated temperature. The XAFS spectrum of In K-edge was recorded on NW10A of PF-KEK. The spectrum was treated by the REX2000 program.

3 Results and Discussion

Fig. 1 shows the Fourier transforms of k^3 -weighted EXAFS spectra of In_2O_3 and $\text{Sc3}/\text{In}_2\text{O}_3$ heated under flowing N_2 at elevated temperature. The spectra of both samples are similar to each other. The spectra at 298 K exhibited three bands at 1.7, 3.1, and 3.6 Å (no phase-shift correction). These bands were assigned to the contributions of In-O and two kinds of In-In. The magnitude of all bands gradually decreased at the higher temperatures, suggesting the disorder of atomic distribution by thermal vibration of a crystal lattice.

The structure parameters calculated from the EXAFS data using the least-square method are summarized in Table 1. The coordination number (CN) of In-O for In_2O_3 is 6.0 at 298 K and then those decreased at higher temperature. This result showed that the oxygen vacancies formed during heat-treatment on the parent In_2O_3 . Such an oxygen vacancy would induce the reduction of In_2O_3 , in particular at the reaction condition such as reductive atmosphere [1]. On the other hand, the CN values of $\text{Sc}/\text{In}_2\text{O}_3$ were constant at even high temperature. For $\text{Sc}/\text{In}_2\text{O}_3$, the formation of oxygen vacancy was greatly prevented. Therefore, the anti-

reducibility of In_2O_3 is improved by the addition of Sc, which resulted in longer lifetimes of the In_2O_3 catalysts [1]. One can suggest that there would be a certain type of surface defects on In_2O_3 which might work as initiation sites of the reduction of oxide during the reaction and that the Sc atoms would be loaded on the sites to prevent the reduction. The similarity of the radius of Sc^{3+} ion of six-coordination, 0.75 Å, to that of six-coordinated In^{3+} ion, 0.80 Å, might support the suggestion.

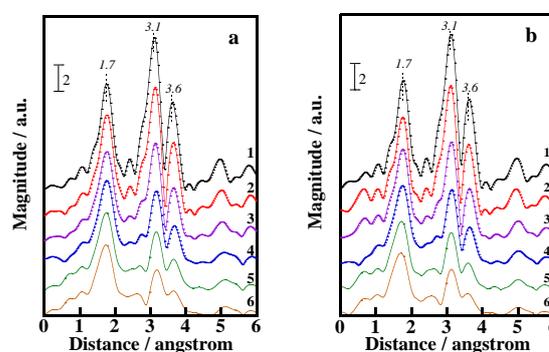


Fig. 1: Fourier transforms of k^3 -weighted EXAFS spectra of (a) In_2O_3 and (b) $\text{Sc3}/\text{In}_2\text{O}_3$ heated under flowing N_2 at elevated temperature. (1) 298, (2) 373, (3) 473, (4) 573, (5) 673, and (6) 773 K.

Table 1: Structure parameters of In_2O_3 and $\text{Sc3}/\text{In}_2\text{O}_3$ heated under flowing N_2 at elevated temperature

		shell	CN ^a	R (Å) ^b	σ^2 (Å ²) ^c
In_2O_3	298 K	In-O	6.0	2.16	4.4×10^{-3}
	373 K	In-O	6.2	2.16	5.2×10^{-3}
	473 K	In-O	6.3	2.16	6.4×10^{-3}
	573 K	In-O	6.0	2.15	6.4×10^{-3}
	673 K	In-O	5.8	2.14	6.9×10^{-3}
	773 K	In-O	5.6	2.14	7.4×10^{-3}
$\text{Sc3}/\text{In}_2\text{O}_3$	298 K	In-O	5.9	2.16	4.2×10^{-3}
	373 K	In-O	6.0	2.16	4.9×10^{-3}
	473 K	In-O	6.0	2.15	5.6×10^{-3}
	573 K	In-O	6.2	2.15	6.9×10^{-3}
	673 K	In-O	6.2	2.14	7.9×10^{-3}
	773 K	In-O	6.1	2.13	8.6×10^{-3}

^a Coordination number. ^b Interatomic distance. ^c Debye-Waller factor.

References

[1] M. Iwamoto *et al.*, *Chem. Lett.* **41**, 892 (2012); *Chem. Eur. J.* **19**, 7214 (2013).

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