

## Structural analysis of La/Al<sub>2</sub>O<sub>3</sub> catalysts by La K-edge XAFS

Takashi Yamamoto,\* Tsunehiro Tanaka, Takahiro Matsuyama, Takuzo Funabiki and Satohiro Yoshida

Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan. E-mail: yamamoto@dcc.moleng.kyoto-u.ac.jp

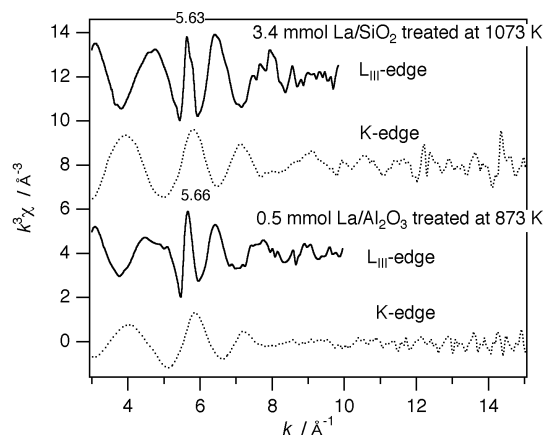
Structural analysis of La/Al<sub>2</sub>O<sub>3</sub> catalyst materials was carried out by means of XRD and La K-edge XAFS. Influences of loading amounts and treatment temperature on the local structure around La were investigated. La atoms are supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in a highly dispersed form when a loading amount is less than 0.2 mmol g(Al<sub>2</sub>O<sub>3</sub>)<sup>-1</sup>, and structural transformation of the La species does not take place in the temperature ranges of 873–1273 K. La species of highly loaded catalysts start to change their structure from oxide-like form to the aluminate at 1073 K. Formation of LaAlO<sub>3</sub> perovskite on the catalyst surface requires a concentration of La atoms above 0.5 mmol g(Al<sub>2</sub>O<sub>3</sub>)<sup>-1</sup> (7.5 wt% as La<sub>2</sub>O<sub>3</sub>).

**Keywords:** La<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, LaAlO<sub>3</sub>, La K-edge XAFS

### 1. Introduction

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> is widely used as a support for industrial catalysts. The phase transformation from  $\gamma$ - to  $\alpha$ -phase and the decrease of the surface area, so called sintering, are serious problems in the use of the catalyst at high temperature. It is well known that addition of lanthanide (Ln) and alkaline earth element to alumina enhances its thermal stability, and there are many studies dealing with the prevention of sintering (Arai & Machida, 1996; Bettman *et al.*, 1989; Burtin *et al.*, 1987; Oudet *et al.*, 1988; Schaper *et al.*, 1983 & 1984). The surface LaAlO<sub>3</sub> phase formed on Al<sub>2</sub>O<sub>3</sub> was proposed to enhance thermal stability of an alumina-based catalyst (Oudet *et al.*, 1988). However, crystalline LaAlO<sub>3</sub> was detected at a loading amount above 16%. The XRD characterization is not effective when a crystalline size was less than 100 Å. Although structural characterizations of La<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts have been carried out by many research groups (Alvarez *et al.*, 1997; Arai & Machida, 1996; Bettman *et al.*, 1989; Capitán *et al.*, 1995; Haack *et al.*, 1992; Oudet *et al.*, 1988; Schaper *et al.*, 1983 & 1984; Shi *et al.*, 1997), it remains unclear whether the perovskite phase forms on alumina only at a loading amount less than 10 wt% or not.

In the present study, we recorded La K-edge XAFS spectra to examine the structure of La species on alumina and their structural transformation upon thermal treatment. In the case of lanthanide, only a restricted information could be obtained from L<sub>III</sub>-edge EXAFS because of the limitation of the L<sub>II</sub>-edge. Especially for La, L<sub>III</sub>-edge EXAFS is available over no more than 10 Å<sup>-1</sup>. Figure 1 shows La K- and L<sub>III</sub>-edge EXAFS spectra of supported lanthanum oxides. As shown in the figure, multi-electron excitation from 2p<sub>4d</sub> to (5d)<sup>2</sup> was observed around 5.6 Å<sup>-1</sup> at L<sub>III</sub>-edges, as in the case of La@C<sub>82</sub> (Nomura *et al.*, 1995). Therefore, characterization with Ln K-edge XAFS instead of L<sub>III</sub>-edge XAFS is very important to obtain detailed structural information. The present study is the first application of lanthanide K-edge XAFS to supported catalyst materials.



**Figure 1**  
La K- and L<sub>III</sub>-edge EXAFS spectra of supported lanthanum oxide.

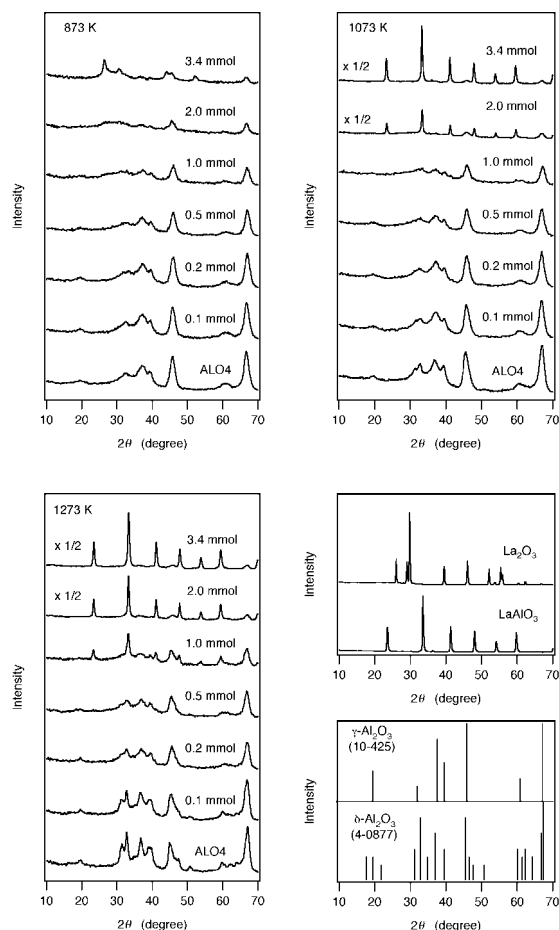
### 2. Experimental

La/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (JRC-ALO4; 174 m<sup>2</sup> g<sup>-1</sup>) with an aqueous solution of La(NO<sub>3</sub>)<sub>3</sub> (Nacalai, 99.9%) at 353 K, followed by calcination at 773 K for 5 h. These samples are referred to as *x* mmol La/Al<sub>2</sub>O<sub>3</sub> (*x* stands for loading amount of La atom per gram of Al<sub>2</sub>O<sub>3</sub>). Prior to XAFS measurements, each sample was evacuated at a prescribed temperature for 0.5 h and calcined under O<sub>2</sub> for 1 h, followed by evacuation at the same temperature for 1 h. The X-ray absorption experiments were carried out on the BL01B1 beamline at SPring-8 (Hyogo, Japan) (Uruga *et al.*, 1999). The ring energy was 8 GeV, and the stored current was 70–100 mA. The La K-edge X-ray absorption spectra were recorded in the transmission mode with a Si(311) two-crystal monochromator at room temperature. Data reduction was performed using a FACOM M1800 computer of Kyoto University Data Processing Center. The normalization method has been previously reported in detail (Tanaka *et al.*, 1988). The Fourier transform was performed on EXAFS in the *k* range of ca. 3.2–14 Å<sup>-1</sup>.

### 3. Results and Discussions

Figure 2 shows XRD patterns of La/Al<sub>2</sub>O<sub>3</sub> catalyst treated at 873, 1073 and 1273 K. At a calcination temperature of 873 K, all patterns except for 3.4 mmol La/Al<sub>2</sub>O<sub>3</sub> exhibited typical lines assigned to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. On the other hand, other lines appeared on 3.4 mmol La/Al<sub>2</sub>O<sub>3</sub> which were not identified with any JCPDS files. The decomposition temperature of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> to La<sub>2</sub>O<sub>3</sub> is 1020 K (Squir *et al.*, 1994). Therefore, the lines were assigned to an intermediate phase between La<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, which was formed at the catalyst preparation step. At a calcination temperature of 1073 K, formation of LaAlO<sub>3</sub> perovskite was confirmed at a loading of 2.0 mmol g(Al<sub>2</sub>O<sub>3</sub>)<sup>-1</sup> and higher. Furthermore, it was confirmed that lanthanum species on 1.0 mmol La/Al<sub>2</sub>O<sub>3</sub> transformed to LaAlO<sub>3</sub> at 1273 K. The alumina-phase of 0.1 mmol La/Al<sub>2</sub>O<sub>3</sub> and the support itself transformed to the  $\delta$ -phase at 1273 K.

Figure 3 shows La K-edge EXAFS spectra and their Fourier transforms (radial structure functions; RSFs) of La/Al<sub>2</sub>O<sub>3</sub> catalysts treated at 873 K. The EXAFS spectra of all catalyst sample treated at 873 K, which loadings were less than 2.0 mmol g(Al<sub>2</sub>O<sub>3</sub>)<sup>-1</sup>, were quite similar with loading and a single peak appeared on the RSF

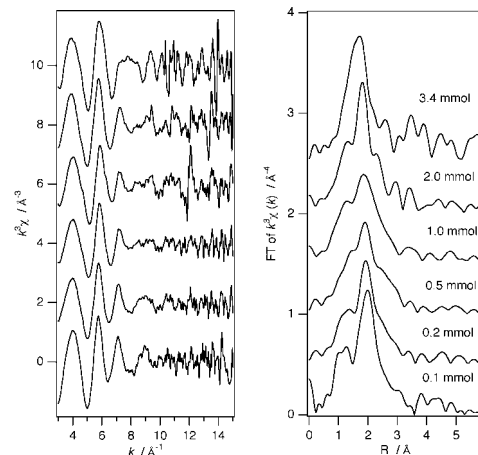


**Figure 2**

Cu K $\alpha$  XRD patterns of La/Al<sub>2</sub>O<sub>3</sub> treated at 873, 1073 and 1273 K, La<sub>2</sub>O<sub>3</sub>, LaAlO<sub>3</sub> and JCPDS files.

around 1.9 Å. The oscillation amplitude decreased monotonously with  $k$ , and little oscillation appeared in the  $k$ -region above 9 Å<sup>-1</sup>, indicating that La species are supported in a highly dispersed form and that no La-(O)-La contribution exists on the catalyst sample. The remarkable degree of decay of the oscillation amplitude should be noted. The natural width ( $\Gamma$ ) of the La K-edge (14.1 eV) is much larger than that of the L<sub>III</sub>-edge (3.41 eV) (Krause and Oliver, 1979). The lifetime of the core hole created by absorbing an X-ray photon can be deduced from the width  $\hbar\Gamma/2\pi$  of the state. The resulting large  $\Gamma$  decreases the amplitude of the EXAFS oscillations (Strans, 1984). Therefore, the amplitude of EXAFS oscillations for the La K-edge should be smaller than that for the L<sub>III</sub>-edge. On the other hand, the EXAFS amplitude of supported Yb species at the K-edge (61.3 keV;  $\Gamma = 31.9$  eV) was stronger than that at the La K-edge (Yamamoto *et al.*). Then, the remarkable oscillation decay at the La K-edge was due to an extremely large apparent Debye-Waller factor, *i.e.*, surface La species (LaO<sub>x</sub>) have many kinds of La-O bond-length, and/or the symmetry of LaO<sub>x</sub> polyhedra on Al<sub>2</sub>O<sub>3</sub> is quite distorted. Existence of many La-O bond lengths might cause counteracting the EXAFS oscillations. The irregular frequencies of EXAFS oscillation support this deduction.

Figure 4 shows EXAFS spectra and their RSFs of La/Al<sub>2</sub>O<sub>3</sub> catalysts treated at 1073 and 1273 K and reference compounds. Crystalline La<sub>2</sub>O<sub>3</sub> and LaAlO<sub>3</sub> perovskite exhibited strong EXAFS oscillations up to 15 Å<sup>-1</sup>, and distinct peaks in their RSFs above 2 Å.

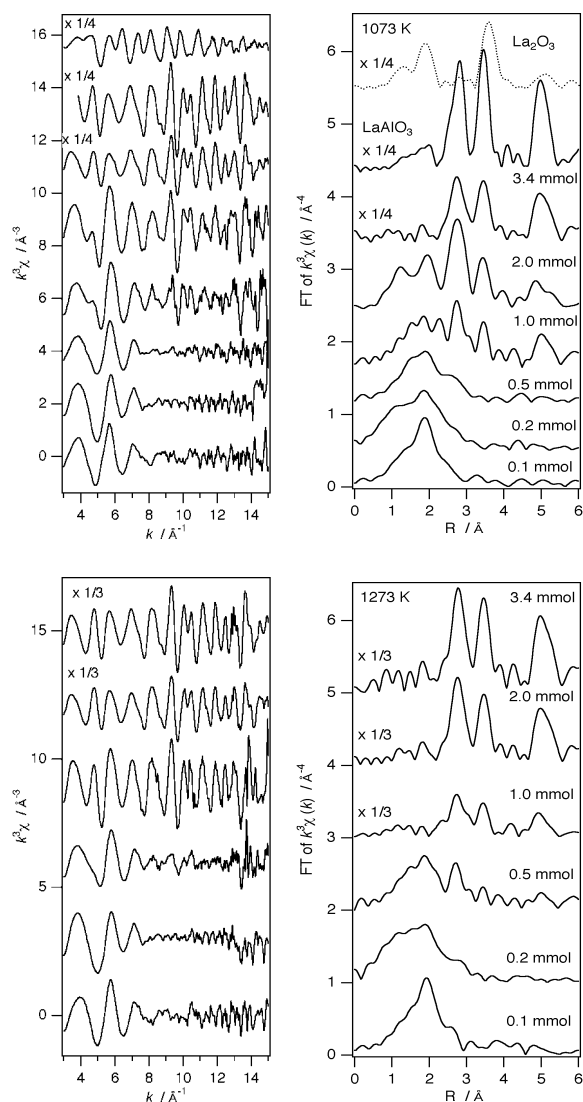


**Figure 3**

La K-edge XAFS spectra and their Fourier Transforms of La/Al<sub>2</sub>O<sub>3</sub> catalyst treated at 873 K.

The EXAFS spectra indicate that La species of catalysts begin to form LaAlO<sub>3</sub> at 1073 K when the loadings were above 1.0 mmol g(Al<sub>2</sub>O<sub>3</sub>)<sup>-1</sup>. At a treatment temperature of 1273 K, formation of LaAlO<sub>3</sub> was confirmed on 0.5 mmol g(Al<sub>2</sub>O<sub>3</sub>)<sup>-1</sup>. On the other hand, the EXAFS spectra of 0.1 and 0.2 mmol La/Al<sub>2</sub>O<sub>3</sub> did not change by thermal treatment up to 1273 K. It shows that La species were supported on Al<sub>2</sub>O<sub>3</sub> in a highly dispersed form without changing their local structure. Therefore, we conclude that formation of LaAlO<sub>3</sub> perovskite on the catalyst surface requires a certain concentration, and that La species at a loading less than 0.2 mmol g(Al<sub>2</sub>O<sub>3</sub>)<sup>-1</sup> are not affected by thermal treatment at a temperature below 1273 K.

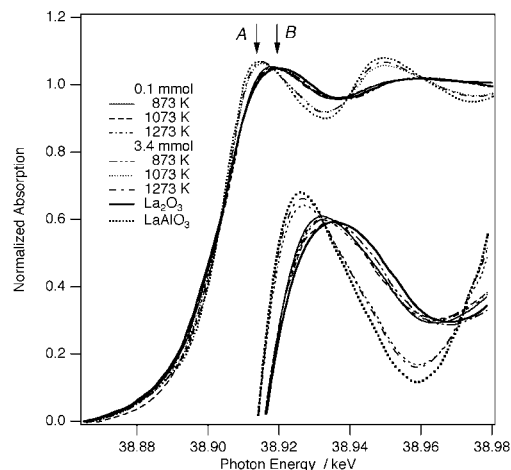
The phase transformation of supported lanthanum species was shown in XANES spectra as well. Figure 5 shows La-K edge XANES spectra of representative catalyst samples, La<sub>2</sub>O<sub>3</sub> and LaAlO<sub>3</sub>. As illustrated with arrows, the energy positions of the first peak were classified to two types. A XANES spectrum of perovskite LaAlO<sub>3</sub> belongs to group A with a lower energy. Those of La<sub>2</sub>O<sub>3</sub> and most of catalyst samples lie in group B with a higher energy although that of La<sub>2</sub>O<sub>3</sub> slightly shifted to higher energy by ca. 2 eV. The positions of the first peak and the configuration for all the La/Al<sub>2</sub>O<sub>3</sub> catalysts (0.1 - 3.4 mmol g(Al<sub>2</sub>O<sub>3</sub>)<sup>-1</sup>) treated at 873 K were the same. The similarity of the XANES spectra indicates that the local structure around La species on Al<sub>2</sub>O<sub>3</sub> resembles that of La<sub>2</sub>O<sub>3</sub>, rather than that of LaAlO<sub>3</sub>. In a case of 3.4 mmol La/Al<sub>2</sub>O<sub>3</sub>, a sample treated at 873 K gave a similar XANES spectrum as that of La<sub>2</sub>O<sub>3</sub>, but those treated above 1073 K exhibited identical spectra to that of LaAlO<sub>3</sub>. This change of XANES spectra upon thermal treatment agrees with the results of the XRD and EXAFS characterizations. It should be noted that the XANES spectrum of 0.1 mmol La/Al<sub>2</sub>O<sub>3</sub> changed hardly by any thermal treatment, in contrast that 3.4 mmol La/Al<sub>2</sub>O<sub>3</sub>. Furthermore, 0.1 mmol La/Al<sub>2</sub>O<sub>3</sub> gave the same XANES spectrum even after thermal treatment at 1473 K. It shows that the local structure of La species on 0.1 mmol La/Al<sub>2</sub>O<sub>3</sub> changed little by thermal treatment, *i.e.*, crystalline LaAlO<sub>3</sub> never forms on La/Al<sub>2</sub>O<sub>3</sub> at a low loading of 0.1 mmol g(Al<sub>2</sub>O<sub>3</sub>)<sup>-1</sup> (1.6 wt% as La<sub>2</sub>O<sub>3</sub>). This is not consistent with a previous ESR characterization claimed that LaAlO<sub>3</sub> forms on 1 mol% La/Al<sub>2</sub>O<sub>3</sub> (3.1 wt% as



**Figure 4**  
La K-edge XAFS spectra and their Fourier Transforms of La/Al<sub>2</sub>O<sub>3</sub> catalyst treated at 1073 and 1273 K.

La<sub>2</sub>O<sub>3</sub>) calcined in air at 1273 K (Schaper *et al.*, 1983). Because the signal intensity of 1 mol% La/Al<sub>2</sub>O<sub>3</sub> was remarkably weak, we assume that only a limited fraction of La species formed LaAlO<sub>3</sub> as ESR active species. A XANES spectrum of 0.5 mmol La/Al<sub>2</sub>O<sub>3</sub> treated at 1273 K was identical to that of 0.1 mmol La/Al<sub>2</sub>O<sub>3</sub>. Since the formation of LaAlO<sub>3</sub> on the surface was confirmed in the RSF, we assume that only a part of the La species on 0.5 mmol La/Al<sub>2</sub>O<sub>3</sub> transformed to the perovskite phase, and that the majority retained the original oxide-like structure after thermal treatment. We conclude that formation of crystalline LaAlO<sub>3</sub> on the catalyst surface requires certain concentration of La atoms, and that highly dispersed La species on Al<sub>2</sub>O<sub>3</sub> hardly form LaAlO<sub>3</sub> perovskite.

Finally, LaAlO<sub>3</sub> has a perovskite structure with cubic symmetry and the first coordination sphere around La consists of twelve oxygen atoms of the same distance (Wyckoff, 1986). Nevertheless, the first peak of LaAlO<sub>3</sub> in the RSF at K-edge was very tiny. On the other hand, a distinct peak appears around 1.9 Å at the L<sub>III</sub>-edge.



**Figure 5**  
La K-edge XANES spectra of La/Al<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub> and LaAlO<sub>3</sub>. Energy was not calibrated.

Such small contribution of the light elements to EXAFS spectra was observed in the RSF of WC at the W K-edge (Borowski *et al.*, 1999). The reason why the first peak of La-O in LaAlO<sub>3</sub> at the K-edge was much smaller than that of La<sub>2</sub>O<sub>3</sub> is unknown.

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