In-situ XAFS study for calcination process of Cr catalyst supported on γ-Al₂O₃ and SiO₂

T Watanabe, K Ikeda, M Katayama* and Y Inada
Department of Applied Chemistry, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan
E-mail: katayama@fc.ritsumei.ac.jp

Abstract. The catalytic performance is largely affected by the oxidation state of supported Cr species, and its control changes the activity of Cr catalysts and the selectivity of products. In this study, the calcination process of the supported Cr catalysts on γ-Al₂O₃ and SiO₂ was investigated by in-situ XAFS spectroscopy. The hydrate species was first supported by the impregnation method and was converted to CrO₃ via Cr₂O₃ during the calcination process on both supporting materials. It was found that the temperature to complete the oxidation from Cr₂O₃ to CrO₃ on SiO₂ was higher than that on γ-Al₂O₃. The similarity of the interatomic distance between the surface oxygen atoms of the intermediate Cr₂O₃ species to that of SiO₂ contributes to the stabilization of Cr₂O₃ on SiO₂ during the calcination process.

1. Introduction

The Cr catalyst supported on SiO₂ is used for the various reactions. For example, ethylene polymerization, dehydrogenation of alkanes, selective reduction of NO, and hydrodesulfurization which are important processes in modern industrial chemistry. Groppo et al. have reviewed about the properties of the Cr/SiO₂ catalyst [1], and the XAFS analysis has been published for the Cr catalyst after the polymerization reaction [2]. The supported Cr catalysts are conventionally prepared by the impregnation method using chromium(II) acetate, chromium(II) chloride, bis(triphenylsilyl)chromate(VI), and chromium(VI) oxide as the precursor materials. It has been reported that the composition of Cr(VI) and Cr(III) species is dependent on the used source materials and that the catalytic activity for the polymerization reaction is enhanced by the existence of the Cr(VI) species on SiO₂ [3]. In addition, a reported speciation for the Cr catalyst using XPS has revealed that the calcination at 300 °C mainly generates the Cr(III) species while the treatment at higher temperature than 500 °C converts the oxidation state to Cr(VI) [4]. The speciation of Cr catalysts of using CrO₃ as a precursor was carried out in calcination process by means of diffuse reflectance spectroscopy, Raman spectra, XAFS, and TPR [5]. The analysis of the oxidation state for the active Cr species is thus fundamental to understand the catalytic performance and to improve its activity. In this study, the in-situ XAFS measurements have been applied to the calcination process of the Cr catalyst to identify directly the chemical state of the Cr species on both γ-Al₂O₃ and SiO₂. A common precursor of chromium(III) nitrate has been used to compare the chemical conversion of the supported Cr species between two supporting materials.
2. Experimental

The powders of $\gamma$-Al$_2$O$_3$ (180 m$^2$/g) or SiO$_2$ (192 m$^2$/g) distributed by the Catalysis Society of Japan were used as the supporting materials, and were suspended in an acidic aqueous solution of Cr(NO$_3$)$_3$·9H$_2$O. The suspensions were dried for 72 h at 50 °C to prepare the precursor samples for the calcination process. The drying at low temperature prevents the chemical state change by the reaction with air for the supported Cr species before the calcination. The Cr loading was set to 5 wt%.

The in-situ XAFS measurements were carried out at the BL-12C station of Photon Factory (KEK, Japan) at the Cr K edge in the transmission mode. The Si(111) double-crystal monochromator was used, and the higher-order harmonics were removed by the Ni-coated double-mirror system. The catalyst precursor powder was set in a flow-type in-situ cell, and the temperature was changed from 25 to 600 °C with the increasing rate of 10 °C/min. During the calcination process, the dilute O$_2$ gas (10 vol% balanced by He) was flowed with the total flow rate of 200 cm$^3$/min as the model condition of the calcination in air. The quick-scanning XAFS measurements were repeated in the X-ray energy range from 5.49 to 7.09 keV with the interval time of 2 min. The background of measured XAFS spectra in pre-edge region was fitted by the Victoreen equation and subtracted from whole region. Then, they were normalized to unit edge step. The composition analysis was carried out for the observed XANES spectrum by the linear combination fitting using those of reference samples with various oxidation states.

3. Results and discussion

The observed XANES spectral change during the calcination process is shown in figure 1 for the Cr species supported on $\gamma$-Al$_2$O$_3$ and SiO$_2$. The XANES spectra of an aqueous solution of Cr(NO$_3$)$_3$·9H$_2$O, a Cr$_2$O$_3$ powder, and a CrO$_3$ powder measured independently are given in figure 1. The initial spectra on both $\gamma$-Al$_2$O$_3$ and SiO$_2$ at 25 °C are identical to that of the aqueous solution of Cr(NO$_3$)$_3$. The existence of [Cr(OH$_2$)$_6$]$^{3+}$ is well established in acidic aqueous solution [6], and the observed XANES spectrum thus confirms that the [Cr(OH$_2$)$_6$]$^{3+}$ species adsorbs on the supporting particle without the modification of the first coordination sphere of the Cr(III) center. The absorption band at the pre-edge region observed in the final XANES spectra demonstrates the oxidation to the Cr(VI) state during the calcination process, and the final spectra are consistent with that of CrO$_3$. The present in-situ XAFS measurements clearly reveal that the initially supported Cr(III) hydrate is converted to the Cr(VI) oxide by heating under the dilute O$_2$ atmosphere. As clearly shown in figure 1, the XANES spectral changes without the isosbestic points suggest the existence of the intermediate species between the Cr(III) hydrate and CrO$_3$.

![Figure 1](image-url)

**Figure 1.** Part (A): Evolution of the XANES spectra of Cr species on $\gamma$-Al$_2$O$_3$ along the calcination process from $T = 25$ °C, blue curve, to $T = 600$ °C, red curve (bottom), intermediate spectra every 20 °C. The top part reports, vertically shifted for clarity, the XANES spectra of CrO$_3$, Cr$_2$O$_3$ and Cr(III) hydrate model compounds. Part (B): as part (A) for Cr species on SiO$_2$. 
The composition analysis based on the XANES spectrum was carried out by the linear combination of three reference species, the Cr(III) hydrate, Cr₂O₃, and CrO₃. The fitting extent of the calculated spectra is represented by R factor:

\[ R = \frac{\sqrt{\sum(\mu_{\text{data}}(E) - \mu_{\text{fit}}(E))^2}}{\sqrt{\sum(\mu_{\text{data}}(E))^2}} \]

where \( \mu_{\text{data}}(E) \) and \( \mu_{\text{fit}}(E) \) are the measured and calculated spectrum, respectively. The observed spectra at 160 °C are compared in figure 2 with the calculated spectra depicted using the estimated mole fraction, and the calculated values of mole fraction are plotted in figure 3 as a function of temperature. The satisfactory reproducibility of the XANES spectrum supports the existence of Cr₂O₃ as the intermediate species on both supporting materials (see figure 2). Figure 3 shows that the Cr(III) hydrate is started to convert to Cr₂O₃ at around 100 °C and that its composition reaches to ca. 40 % at 150 °C. This changeover accompanying the dissociation of bound water molecules is independent of the supporting material. Further increase in temperature promotes the oxidation from Cr₂O₃ to CrO₃ on both supporting materials. The composition of CrO₃ begins to increase at 150 °C and the oxidation is completed up to 250 °C on \( \gamma \)-Al₂O₃ under the present experimental condition. It is marked contrast that the completion temperature of the oxidation to CrO₃ on SiO₂ is much higher than that on \( \gamma \)-Al₂O₃, although the formation temperature of ca. 150 °C is in accordance with that on \( \gamma \)-Al₂O₃. The composition of Cr₂O₃ is kept almost constant (ca. 25 %) in the temperature range from 200 to 400 °C on SiO₂ as shown in figure 3(B). The comparison between \( \gamma \)-Al₂O₃ and SiO₂ clearly indicates the relative stability of the Cr₂O₃ species on SiO₂ rather than on \( \gamma \)-Al₂O₃.

Figure 2. The observed (solid line) and the calculated (broken line) XANES spectrum at 160 °C on \( \gamma \)-Al₂O₃ (A) and SiO₂ (B). The calculated spectra are depicted using the determined mole fractions of Cr(III) hydrate, Cr₂O₃, and CrO₃.

Figure 3. The mole fraction of Cr(III) hydrate, Cr₂O₃, and CrO₃ as a function of temperature on \( \gamma \)-Al₂O₃ (A) and SiO₂ (B).
The crystal structures of $\gamma$-Al$_2$O$_3$ and SiO$_2$ are compared in figure 4 with that of the intermediate Cr$_2$O$_3$ species. The interatomic distance between the surface oxygen atoms is 2.79 Å for $\gamma$-Al$_2$O$_3$ with the defective spinel structure [7], while that of SiO$_2$ is 2.62 Å [8]. The corundum structure of Cr$_2$O$_3$ has two different distances of 2.62 and 2.99 Å as shown in figure 4 [9]. Because it is considered that the supported Cr oxides interact with the supporting material via the oxygen atoms, the similarity of the arrangement of the surface oxygen atoms may contribute to the stabilization of supported Cr species. The stabilization of Cr$_2$O$_3$ species is explained by that both SiO$_2$ and Cr$_2$O$_3$ have the interatomic distance of 2.62 Å. In the case of $\gamma$-Al$_2$O$_3$, it is considered that the mismatch of the interatomic distance leads to the easy conversion to CrO$_3$.

Figure 4. The crystal structures of $\gamma$-Al$_2$O$_3$, Cr$_2$O$_3$, and SiO$_2$.

4. Conclusions
The present in-situ XAFS study for the calcination process of the supported Cr catalysts revealed the chemical state changeover from the initial Cr(III) hydrate to the final CrO$_3$ species via the Cr$_2$O$_3$ intermediate on $\gamma$-Al$_2$O$_3$ and SiO$_2$. It was evaluated that the stability of Cr$_2$O$_3$ was significantly affected by the atomic arrangement of surface oxygen atoms, and the similar interatomic O–O distance between Cr$_2$O$_3$ and SiO$_2$ contributed to the relative stability of Cr$_2$O$_3$ on SiO$_2$ in the temperature range from 200 to 400 °C. A selection of calcination temperature and supporting materials may change the oxidation state of the supported Cr species. Therefore, the Cr catalyst can be designed with the required oxidation state for a catalytic reaction.

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