

Characterization of Supported Chromium Species on Alumina

Akiyuki Ohta, Maiko Utsumi, Yasuyuki Miyake, Shohei Yamashita,
Misaki Katayama, and Yasuhiro Inada

Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan

1. Introduction

The Cr catalyst supported on alumina is used for the polymerization of alkene to produce the low- and high-density polyethylene, and it has been reported that the activity and the selectivity is dependent on the oxidative and reductive pretreatments of the catalyst. The performance variation has been also known for the catalytic dehydrogenation of alkane. Furthermore, the conversion efficiency for the oxidative dehydrogenation of alkane is changed by the Cr loading and the calcination temperature. All these results suggest that the supported Cr species is varied by the preparation conditions, and it is thus very important to characterize the Cr species in the atomic level under the preparation conditions. In this study, the chemical states of the Cr species have been analyzed by means of the XAFS spectroscopy for samples with some different loadings of Cr. The fluorescence XAFS technique has been applied for the dilute samples, because the statistical accuracy is not enough for the conventional transmission measurements. Furthermore, the changeover of the Cr species has been evaluated by means of the *in-situ* XAFS measurements during the temperature-programmed reduction process.

2. Experimental Section

The acidic aqueous solution of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Wako) was dried over γ -alumina (Nikki, $180 \text{ m}^2/\text{g}$) to prepare the Cr catalyst supported on alumina by the impregnation method. The obtained powders were dried at 393 K and were calcined at 773 K in air for 16 h. A part of the calcined sample was treated under the diluted hydrogen atmosphere at 873 K as the reduction procedure.

The XAFS spectra at the Cr K edge were measured at BL-3 of the SR Center, Ritsumeikan University in the transmission mode for samples with the Cr loading of 1 and 3 wt.%. The incident and transmitted X-ray intensity was measured by the ionization chambers flowed by the mixture gas of N_2 and Ar. The fluorescence XAFS measurements were carried out at the same beamline for more dilute samples by using the 3-elements solid-state detector. The reduction process under the diluted hydrogen atmosphere was subjected by the *in-situ* XAFS measurement in the temperature range from 303 to 923 K.

3. Results and Discussion

The XANES spectra of the calcined and reduced samples with the variable loading of Cr are summarized in Fig. 1, in which those of the standard samples are given for comparison. A pre-edge peak

observed at 5992 eV is characteristic for the Cr(VI) species, and thus the valence state of the Cr species supported on γ -alumina is concluded to be +6 after the calcination in air and is independent of the loading of Cr in the range from 0.1 to 3 wt.%. The treatment under the diluted hydrogen atmosphere at the elevated temperature reduces the Cr(VI) species to the Cr(III) state for samples with relatively high loading (1 and 3 wt.%) of Cr as clearly seen in Fig. 1. The XANES feature of these samples is similar to that of Cr_2O_3 . In contrast, the reduction from Cr(VI) to Cr(III) is inhibited as increasing the Cr loading. The pre-edge peak is slightly observed for the sample of 0.5 wt.%, and becomes clear for the sample of 0.1 wt.% (see Fig. 1). It is thus demonstrated that the dispersion of the Cr species increases the resistance to the reduction by hydrogen, indicating that the interaction between the Cr_2O_3 particle and the γ -alumina surface is strong for the smaller Cr_2O_3 particle.

The XANES spectral change is shown in Fig. 2 during the temperature-programmed reduction process. The changeover from Cr(VI) to Cr(III) is successfully followed by the *in-situ* XAFS measurement. Some isosbestic points are clearly observed in the spectral change, suggesting that the existence of intermediate valence states, such as Cr(V) and Cr(IV), is almost negligible because of their relative instability. In Fig. 2(B), the observed X-ray absorbance at 5992 eV (pre-edge peak characteristic for Cr(VI) species) is plotted versus temperature. The absorbance is gradually decreased at lower temperature than 650 K, and the feature of Cr(VI) is remained in the XANES spectrum at such temperature range, suggesting that the surface species of the Cr(VI) particle is reduced to Cr_2O_3 . The bulk of the Cr(VI) particle is reduced at around 680–700 K, at which the pre-edge peak characteristic for the Cr(VI) species is suddenly diminished. The formed Cr_2O_3 particle is stable up to at least 930 K and further reduction is not observed.

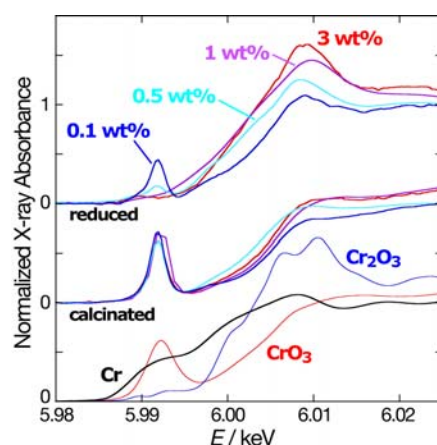


Fig. 1: XANES spectra of supported Cr species after calcination and reduction for variable loading of Cr on γ -alumina.

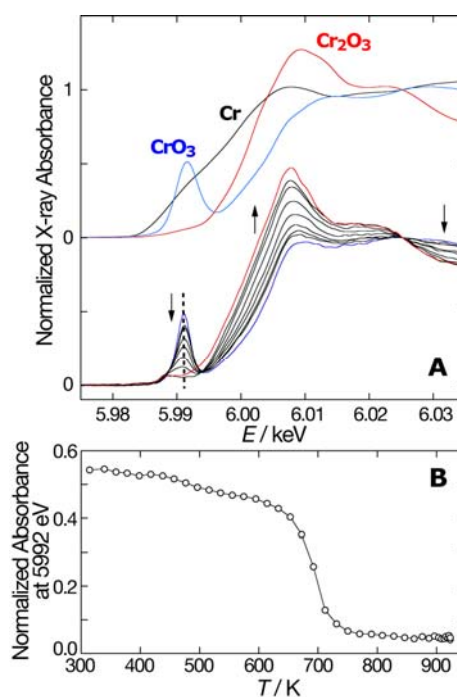


Fig. 2: XANES spectral change (A) and X-ray absorbance change (B) at 5992 eV during the temperature-programmed reduction process under diluted hydrogen atmosphere from 303 to 923 K. The loading of Cr was 3 wt.%.