

Electron Microscopy of Cr/Silica Catalyst for Ethylene Polymerization

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The Phillips Cr/silica catalyst is one of the most important commercial catalysts for the polymerization of ethylene [1]. It has been extensively studied and yet even today there is still debate about the fragmentation mechanism of the catalysts and the valence state of the active chromium sites. We will use environmental transmission electron microscopy (E-TEM) to observe the polymer growth on the nanometer scale. We will also determine the valence state of the active chromium sites. Here we report some preliminary results on the ex-situ catalysts characterization and associated technique development.

The catalyst was prepared by impregnating the 955 silica support (pore volume 1.62 c.c./g and surface area 310 m²/g) with chromium acetate and then calcining in dry air at 825°C for 4 hours to activate. The microstructure (fig. 1) of the Cr/silica catalyst (with 0.5 wt% Cr loading) before activation was determined with a Phillips CM 200 FEG transmission electron microscope. Each microparticle of the catalyst is an agglomeration of small silica particles with an average diameter of about 10 nm. The sample appeared to be amorphous everywhere. No crystalline area, indicating clustering of the chromium compound particles, was found indicating the presence of highly dispersed Cr. It does not appear to be any different from the microstructure of the plain silica, as would be expected.

We will use the technique of electron energy loss spectroscopy (EELS) to determine the oxidation state of Cr during catalysis.[2] In our research, it is necessary to determine the oxidation state of very small amounts of Cr in the presence of a large O edge from the underlying silica support. We have compared three different methods for determining the Cr valence states from two Cr standards of known oxidation state: Cr₂O₃ (Cr⁺³) and PbCrO₄ (Cr⁺⁶). Energy-loss spectra were acquired in a Phillips 430 E-TEM operating at an accelerating voltage of 300 kV. The spectra are shown in fig. 2 with the first peaks of the oxygen K edge aligned with each other.

Table 1 shows that ΔE_1 and ΔE_2 (the position of the maximum intensities of the Cr-L_{2,3} absorption edges relative to the first peak of the O-K edge) increased by about 4 eV with increasing oxidation state. About 2/3 of this change in ΔE_1 and ΔE_2 was caused by the chemical shift of Cr-L_{2,3} edges (2.7 eV reported by Daulton et al.[3]) and the rest of the change was caused by the chemical shift of the O-K edge. The L₃/L₂ white-line ratio, i.e. I(L₃)/I(L₂), was determined after first subtracting an AE^T background from beneath both O and Cr edges and then subtracting a trapezoidal region from under the Cr white-line region to make a first order correction for transitions to the continuum states above the thresholds of these edges. The results show that the I(L₃)/I(L₂) ratio decreases with increased oxidation state. Finally we tried determining the valence state by normalizing the total white-line intensity to the continuum I(C) in a window 50 eV in width beginning 50 eV past the L₃ white line onset. The contribution of O signal in this normalization window was approximated using the calculated O energy differential cross-section and subtracted (illustrated in fig. 2). Since the accuracy of this method strongly depends on the quality of both the background subtraction and the calculated differential cross-section, it was believed to cause a

big error range although the data show that the normalized white-line area increases with increased oxidation state. Therefore the oxidation state of Cr in the catalyst can be best determined by the chemical shift of $L_{2,3}$ edges relative to the first peak of O-K edge from silica and the ratio of $I(L_3)/I(L_2)$, integrated-peak intensities. An *in-situ* polymerization experiment will be performed in an environmental transmission electron microscope (a modified Phillips 430 E-TEM) to observe the evolution in the catalyst microstructure and the chromium oxidation state.

References

- [1] K. H. Theopold, *European Journal of Inorganic Chemistry* 1 (1998) 15.
- [2] D. H. Pearson et al., *Phys. Rev. B* 47 (1993) 8471.
- [3] T. L. Daulton et al., *Microscopy and Microanalysis* 7 (2001) 470.
- [4] Funding was provided by the Dow Chemical Company and the Industrial Associates Program of Arizona State University.

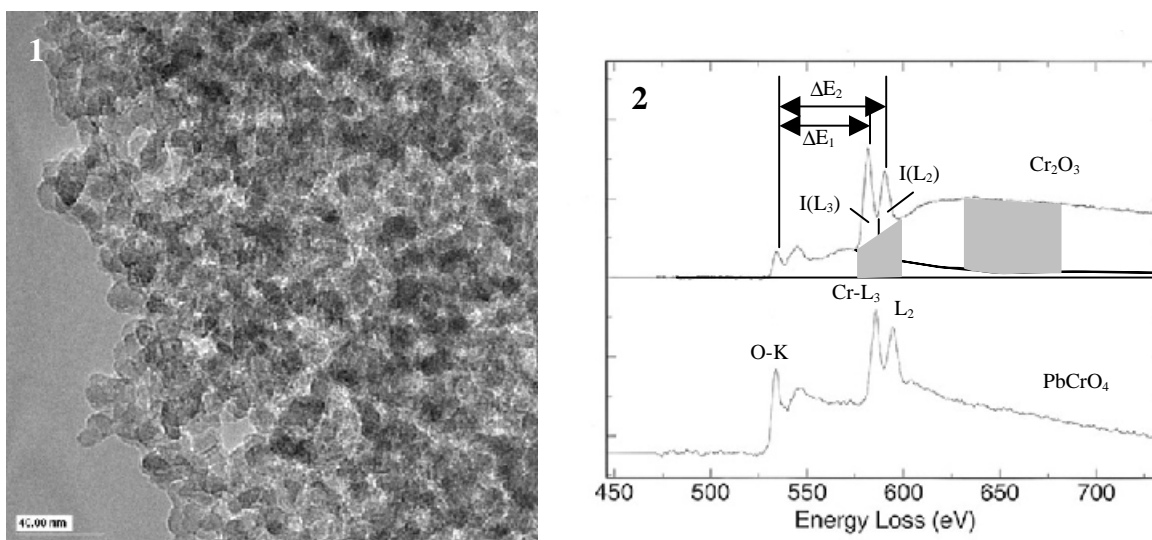


FIG. 1. TEM picture of the Cr/silica catalyst showing the agglomeration of small SiO_x particles.

FIG. 2. EELS spectra from Cr_2O_3 (Cr^{+3}) and PbCrO_4 (Cr^{+6}), with the first peaks of O-K edge aligned with each other. The method for isolating and normalizing the Cr white-line intensities $I(L_3)$ and $I(L_2)$ is also shown (see text).

Table 1 Results from three EELS processing techniques showing their sensitivity to the oxidation-state-induced change in two Cr standards, see text.

Compound	Cr valence	ΔE_1 (eV)	ΔE_2 (eV)	$I(L_3)/I(L_2)$	$(I(L_3)+I(L_2))/I(C)$
Cr_2O_3	+3	47.5 +/- 0.5	56.0 +/- 0.5	1.52 +/- 0.03	0.25 +/- 0.06
PbCrO_4	+6	51.5 +/- 0.5	60.5 +/- 0.5	1.23 +/- 0.06	1.4 +/- 0.8