

An *in-situ* EELS study of Co-based Fischer-Tropsch Catalysts

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The study of Co nano-particles has drawn increasing attention due to their importance in many catalytic reactions, such as Fischer-Tropsch (FT) synthesis. While it is commonly accepted that the presence of metallic surfaces is crucial to the catalytic activity of Co nano-particles, it was recently reported that the addition of small amounts of Mn has a dramatic effect on the catalyst's activity and selectivity. One possible reason is that the presence of Mn prevents the complete reduction of Co catalyst-particles. It is therefore of great interest to develop a method for identifying metallic Co and Co-oxides in nano-scale particles with atomic resolution. In this presentation, we will report a detailed analysis of metallic Co and Co-oxide (CoO and Co₃O₄) nano-particles using a combination of Z-contrast imaging, electron energy-loss spectroscopy (EELS) and *in-situ* heating experiments, as well as first-principles density functional theory (DFT) calculations using the CASTEP code. Based on our experimental and theoretical results, we propose a six-Gaussian fitting method to distinguish metallic Co from any Co-oxides. [1-3]

Figure 1 shows the O K-edge and Co L-edge of metallic Co, CoO and Co₃O₄. The metallic Co sample was *in-situ* reduced at 450°C for 10 hours prior to any data acquisition. The O K-edge fine-structure shows significant differences between CoO and Co₃O₄, while the extracted Co L₃/L₂-ratio is found to be 3.15 (Co), 4.51 (CoO) and 2.42 (Co₃O₄). No O signal is found in metallic Co sample. In Figure 2, a comparison of the Co L-edges from metallic Co and partially-reduced Co₃O₄ particle with the same L₃/L₂-ratio is shown. It can be seen that the areas labeled *c* and *e* exhibit significant higher intensity in the Co spectrum compared to the Co-oxide. A combination of 50% CoO and 50% Co₃O₄ reference spectra fit the Co-oxide well, but could not fit the Co metal. Figure 3 shows a comparison of calculated Co L₃ edges for metallic Co and Co₃O₄. It can be seen that the intensity of transition $2p \rightarrow 4s$ orbital in simulated metallic Co L-edge is twice as much as in the Co-oxide. Experimental and theoretical metallic Co L-edges are also compared, indicating that the increased intensity between the L₃ and L₂ edges (position *c* in Figure 2) is due to the larger contribution of transition $2p^{3/2} \rightarrow 4s$. Based on these findings, we proposed a method to fit the metallic Co L-edge using only 2 parameters. Figure 4 shows the result of our proposed method, which contains six Gaussian peaks and Co Hartree-Slater ionization cross-section to fit the shape of metallic Co L-edge.

In this presentation, we will demonstrate that using our reference spectra of Co, CoO, and Co₃O₄, we can now determine the local composition of heterogeneous Co nano-catalysts. Figure 5 shows a spectrum extracted from a Mn/Co/TiO₂ FT catalyst. We find that Co particle has a core-shell structure with 55% Co in the core, as well as 25% CoO and 20% Co₃O₄ in the shell. [4]

References

- [1] Y. Zhao, T. E. Feltes, J. R. Regalbuto, R. J. Meyer, R. F. Klie, Physical Review B (*submitted*)
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- [3] M. J. Keyser, R. C. Everson, and R. L. Espinoza, Applied Catalysis a-General **171**, 99 (1998)
- [4] This research is supported by the American Chemical Society Petroleum Research Fund.

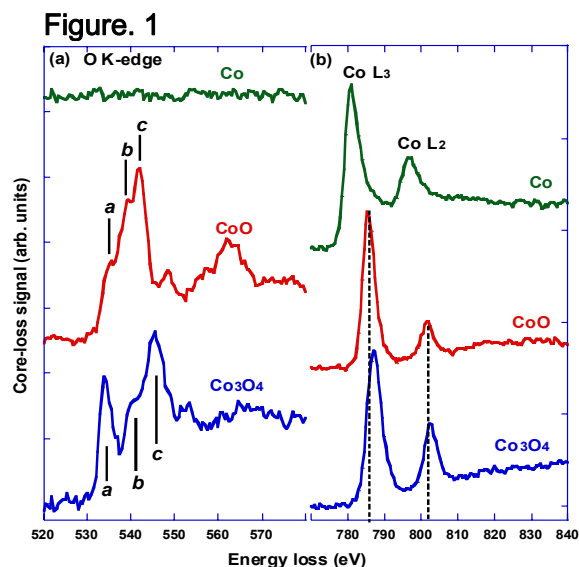


Figure.1(Color). Comparison of (a) O K-edges and (b) Co L_{2,3} edges of metallic Co, CoO and Co₃O₄.

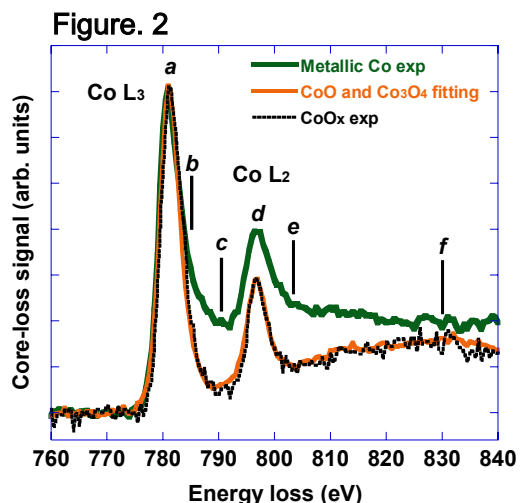


Figure.2 (Color). Co L-edges of metallic Co and Co-oxide samples. A linear combination of 50% CoO and 50% Co₃O₄ (orange line) was used to fit the experimental data.

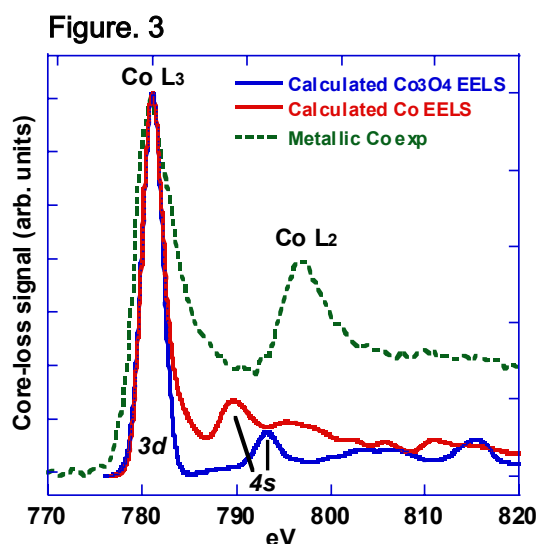


Figure.3 (Color). Comparison of theoretical Co₃O₄ and Co L₃-edges, and experimental Co L-edge.

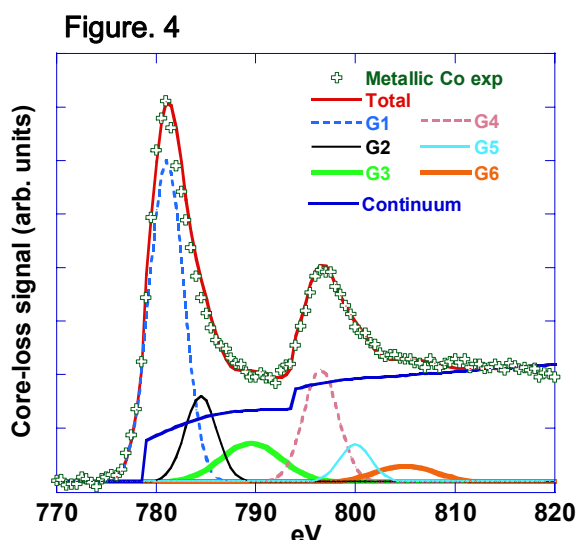


Figure.4 (Color). Co L-edges of metallic Co, and a fitting to the experimental data by using six-Gaussian functions (G1-G6) and a Hartree-Slater cross-section.

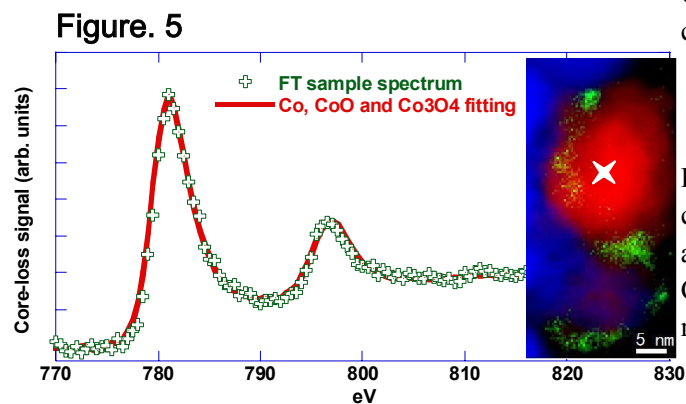


Figure.5 (Color). Co L-edges (acquired at the white cross position) of the reduced Co-based FT catalyst and the fitting result of 55% Co, 25% CoO and 20% Co₃O₄. In the SI RGB map, red represents Co, green represents Mn, blue represents Ti.