

## Aberration-Corrected ETEM: In-Situ Reduction of Cobalt Oxides

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Understanding the dynamic evolution of structural changes in catalysts under controlled reaction conditions at the atomic level is important in heterogeneous catalysis. Supported cobalt based nanoparticles are of interest in a number of hydrogenation reactions including Fischer-Tropsch (F-T) process for synthetic fuel technologies and environmental control. Fe based catalysts are reported to be selective for some alkanes at high temperatures of 350°C. More recently, Co based catalysts have been used because they offer a compromise between cost, efficiency and selectivity for linear hydrocarbons at low temperature of 225°C [1]. The Co catalysts have been found to be highly selective including for C<sub>5+</sub> hydrocarbons which is beneficial for the synthesis of diesel. However direct nanostructural studies to understand the factors influencing the activity are limited. Based on chemical methods and activity measurements active sites in the F-T process have been reported to be Co<sup>0</sup> (Co metal) [1]. Typical F-T catalysts use Co nanoparticles on supports such as Al<sub>2</sub>O<sub>3</sub> but the metal loading can be often above 33% to encourage a high level of activity as well as selectivity.

The uncertainties surrounding the activity of Co based catalysts may originate from the catalyst activation process. Co is rarely available as a pure metal for the development of catalysts. Instead, an oxide, usually Co<sub>3</sub>O [2], is reduced by pre-treatment in H<sub>2</sub> and N<sub>2</sub>. The nature of the reduction of the oxide ultimately determines the range of reduced/oxidised Co species in the catalyst. These play a key role on the structure, morphology and the activity of the catalyst. However the dynamic reduction mechanism of the oxide at the atomic level is not well understood. Literature reports [2] show a two stage reduction process of Co<sub>3</sub>O<sub>4</sub> : Co<sub>3</sub>O<sub>4</sub> → CoO → Co.

Here we present aberration corrected environmental transmission electron microscopy (AC-E TEM) at the atomic level [3,4] of the reduction of model Co<sub>3</sub>O<sub>4</sub> catalysts in H<sub>2</sub> to directly observe the dynamic phase evolution in the reduction process. New insights into the reduction mechanism from Co<sub>3</sub>O<sub>4</sub> to the intermediate CoO reveal the formation of an advancing atomic scale interface between the Co<sub>3</sub>O<sub>4</sub> and CoO regions (FIG.1). The interface is observed to extend into the Co<sub>3</sub>O<sub>4</sub> crystal with the CoO regions replacing the previous Co<sub>3</sub>O<sub>4</sub> structure with increasing reduction. Atomic level interfacial dislocations [5] are also observed. The reduction to CoO is observed to proceed at ~ 200°C at rounded edges containing atomic steps at the surfaces. The interfaces are observed in crystals above about 15 nm in size but not in smaller crystals, suggesting the rapid reduction of smaller nanoparticles. The most dramatic changes are observed at 350 °C in larger crystals of 50 nm.

### References

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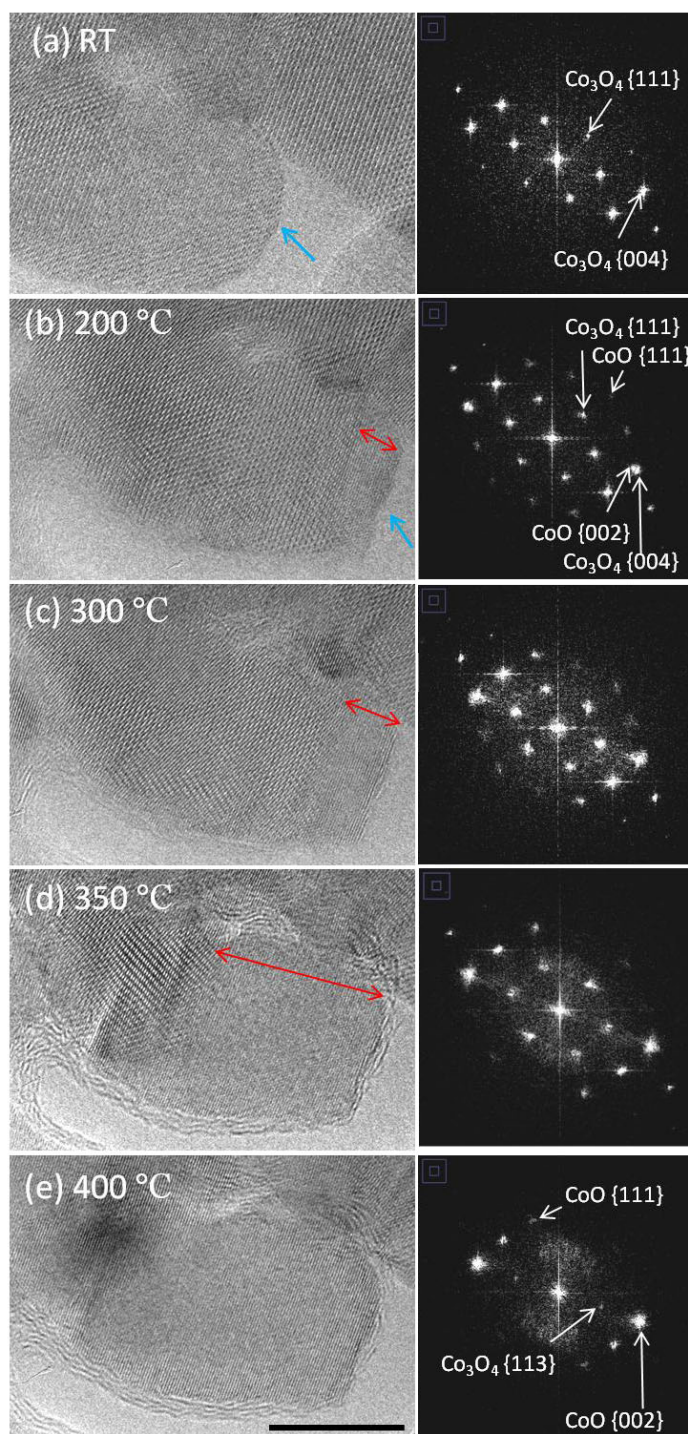


FIG.1 Dynamic AC-ETEM atomic level sequence with corresponding FFTs in hydrogen gas as a function of reaction temperatures (a-e), showing the transformation of  $\text{Co}_3\text{O}_4$  to  $\text{CoO}$ . The  $\text{Co}_3\text{O}_4$  {004} and  $\text{CoO}$  {002} spacing's are very similar. The FFTs imply that the crystal is about  $4^\circ$  away from the exact  $\text{Co}_3\text{O}_4$  and  $\text{CoO}$  [110] zone axis. The blue arrow shows that the rounded facet has become almost flat. The red arrow shows dimensions of  $\text{CoO}$  region. The scale bar in (e) is 10 nm.