Operando TEM Enables Direct Correlation of Catalyst Surface Structures and Activity

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Introduction

CO oxidation over transition metal catalysts has been studied extensively at a fundamental level. Despite this, the most active form of Ru catalysts for CO oxidation is still debated [1,2]. *Operando* transmission electron microscopy (TEM) is an emerging technique with the potential to directly observe the structure of catalyst nanoparticles while simultaneously measuring the relative activity of the catalyst by continuously monitoring the gas composition. We use *operando* TEM to observe the subtle changes in surface structure which accompany changes in catalytic activity.

Materials and Methods

Two complimentary techniques have been used to determine the gas composition inside the environmental TEM (ETEM) cell: electron energy-loss spectroscopy (EELS) and residual gas analysis (RGA) [3]. A novel TEM sample preparation method was also used in which the supported catalyst is dispersed over both a pyrex fiber pellet and a wire mesh grid, which are loaded together into a Gatan Ta furnace heating holder.
CO oxidation was performed over a silica-supported Ru catalyst. Ru particles are between 5 and 15 nm in diameter and the amorphous silica spheres on which they are supported are approximately 200 nm in diameter. *Operando* TEM experiments were performed on an image corrected FEI Titan ETEM.

Results and Discussion

Experiments performed in a plug-flow reactor have shown a hysteresis in the CO conversion of this Ru catalyst, as seen in the inset of Figure 1. It appears that the low temperature activity of the catalyst is somehow enhanced after exposure to conditions giving conversions close to 100% around 250 ºC. This observation is essential for interpreting recent *operando* TEM experiments which also showed a hysteresis in the CO conversion as pointed out in Figure 1.

The CO conversion during the *operando* experiment was measured and compared to a calculation of the expected conversion for a catalyst of constant activity. This calculation was based on a fit of the *ex-situ* reactor data. From this comparison, it is clear that the catalyst is more active at time A after the high temperature condition (Figure 1). This activity change would have been missed in a simple *in-situ* experiment, in which the CO conversion would not be measured. Comparing images of the same particle observed at points A and B, shown here in Figure 2, it is clear that the particle at time A (more active) has a clean Ru metal surface, while the particle at time B (less active) has oxide layers on the surface. Thus, RuO_2 layers are correlated with lower activity. This contradicts the conclusions of a number of papers which had claimed that thin RuO_2 layers were the most active structure for CO oxidation [1]. This work clearly demonstrates the benefit of *operando* experiments over *in-situ* studies and emphasizes the importance of performing *ex-situ* reactor experiments in parallel.

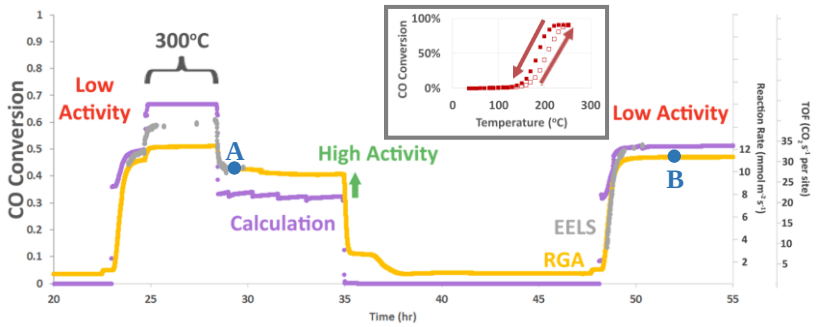

Figure 1. *Operando* TEM experimental data compared with a calculation based on the *ex-situ* data shown in the inset. Both the *ex-situ* data and the *operando* data demonstrate the higher activity of the Ru catalyst following a period of high temperature and high conversion.

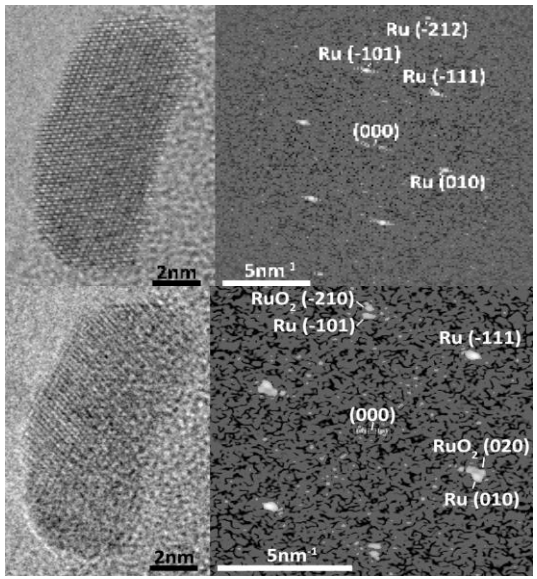

Figure 2. Top: Image and processed FFT of a nanoparticle at time A, (labeled in Fig 1) showing clean Ru metal surfaces. Bottom: Image and processed FFT of the same nanoparticle at time B, showing evidence of RuO_2 layers formed on the surfaces of the nanoparticle.

Significance

A direct correlation between catalyst structure and activity is possible using *operando* TEM which is shown to be preferred over *in-situ* TEM, a technique that would likely have led to the wrong conclusion in this case.

References

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4. This work was supported by The National Science Foundation (NSF-CBET 1134464).