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We have investigated the structure of a Re_4Co catalyst which is highly active for ammonia synthesis at ambient pressure. For this work we utilised an *in situ* cell up to 600°C with XAS and XRD being obtained throughout the entire reaction in order to elucidate the speciation of cobalt and rhenium during the reaction. Also *ex situ* standards were analysed with XAS in order to accurately determine specific oxidation state changes of rhenium and cobalt during the reaction. *In situ* XAS measurements were performed at the cobalt *k*-edge and rhenium L_3 edge.

Experimentally, the Re_4Co material was pre-treated for 2 hours under H_2/N_2 (1:3) from room temperature to 600°C using a ramp rate of $10^\circ\text{C}/\text{min}$ and flow rate of $60\text{ ml}/\text{min}$. Next the temperature was reduced and ammonia synthesis reaction performed under H_2/N_2 at 400°C . XAS and XRD scans were collected throughout the entire reaction. The procedure was then repeated using Ar/H_2 as the pre-treatment gas mixture and H_2/N_2 was switched in at 400°C for the ammonia synthesis reaction.

We were able to specifically pin point the periods in the reaction profile in which significant changes in the material occur. Then apply this knowledge to acquire high speed EXAFS scans (one scan every ca. 6 seconds) to enable us to follow the reduction of the rhenium precisely (Figure 1).

Using a range of standards it was possible to elucidate the oxidation state changes of Co and Re during each stage of the reaction. It was found rhenium starts in the +7 oxidation state and reduces to metallic rhenium at ca. 500°C (Figure 2) and remains in a 0 oxidation state throughout the entire reaction.

Figure 3 shows XRD data for the material during different temperatures/time during the reaction. The availability of *in situ* XRD was highly beneficial to the project as it allows us to follow changes in the structure of the catalyst in the reactor.

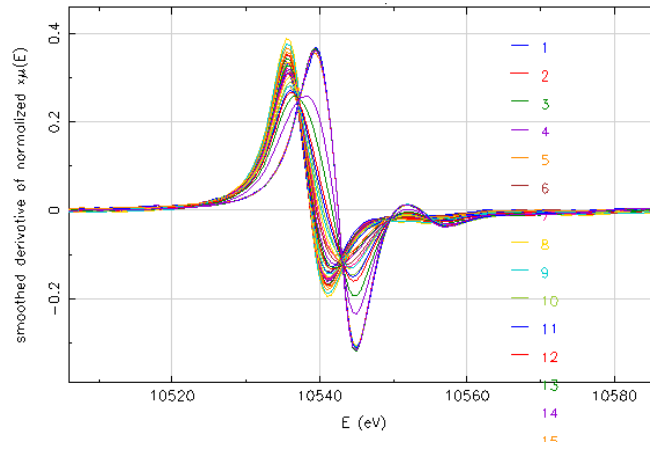


Figure 1: High Speed EXAFS on Re L3 Edge

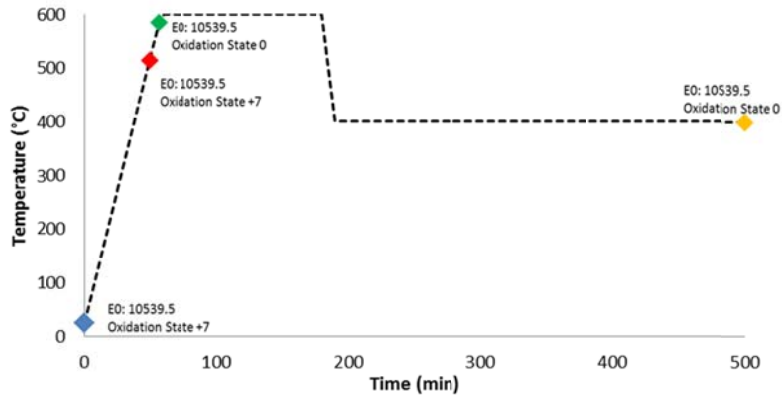


Figure 2: Rhenium Oxidation State Changes throughout Reaction Profile

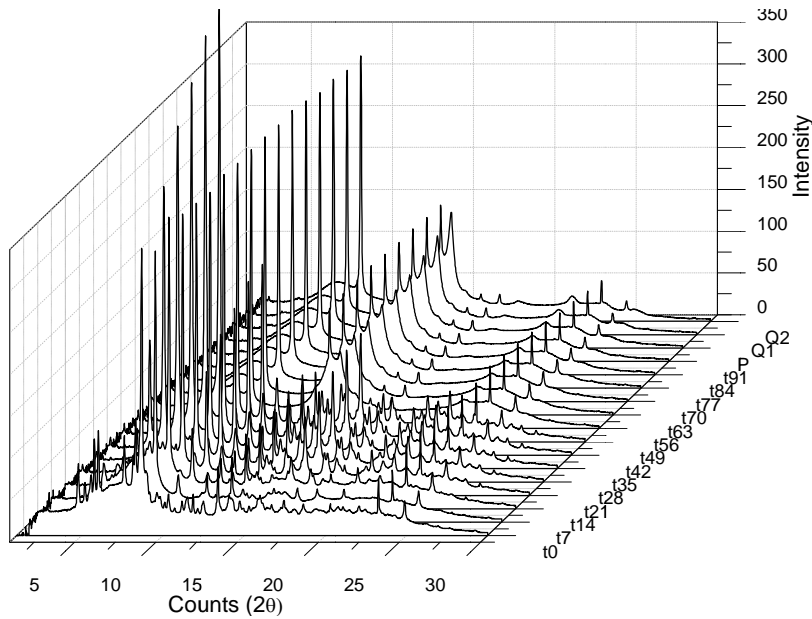


Figure 3: In Situ XRD for Re_4Co