Structure and Redox chemistry of Ceria and metal promoted Ceria: An in situ PDF investigation

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Ceria is widely used as support material in catalytic applications. The aim of this experiment is to use total X-ray scattering techniques to determine the geometric structure of ceria during reaction with air, hydrogen and inert gases, in particular nitrogen. Recent studies on these systems show that reduction of ceria takes place at temperatures above 500^{o}C (in the absence of any metal particles) in hydrogen and at much lower temperatures depending on the type of metal present in the system. We focused our study by measuring total scattering data at ID15, as a function temperature.

Numerous PGM loaded ceria samples with different level of loadings were prepared at the Johnson Matthey laboratories. These powder samples were then pelletised, breaking them into small pieces and sieving them in order to obtain similar sized grains which allow the gas flow. Typical experimental setup is shown in figure 1; the capillary reactor was designed and fabricated at University College London and mounted on a standard hot-air furnace available at ESRF

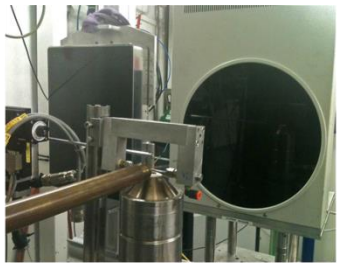

Figure 1: The setup for the in-situ studies of ceria based catalytic materials. This capillary setup also allows the use of different gases and use of different materials.

Following samples were measured under reaction conditions. Ceria without metal, 5 and 10 wt% Pd on ceria and 5 wt% Pt on ceria were investigated during the reaction with hydrogen (5% H2/95% N2). Samples were heated at 5^{o}C/min from room temperature to 450^{o}C and cooled in either hydrogen or nitrogen whilst taking a scan every minute.

All the XRD data were processed using GSAS Rietveld refinement software. The converted PDF data (G(r)) were refined using the PDFgui software, and the initial analysis was restricted a r range of ca 2 to 15 Å. Typical XRD (Q vs S(Q)) and the PDF (r vs G(r)) are shown in Figure 2.

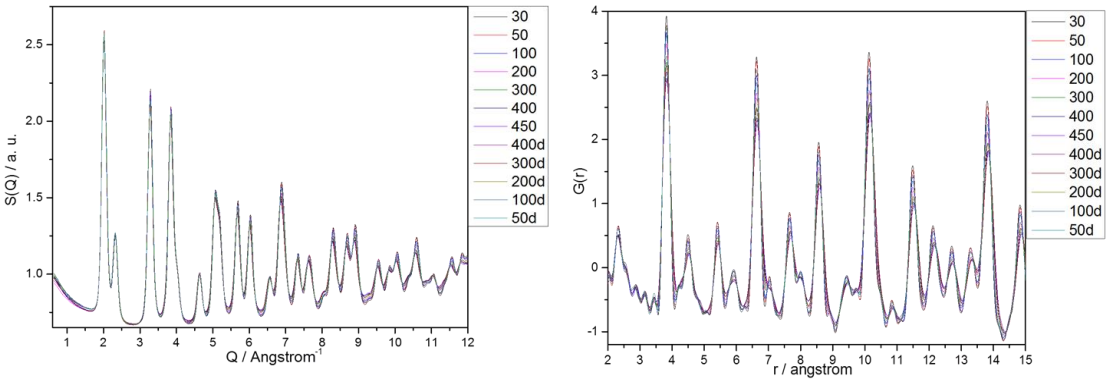

Figure 2: Typical XRD (S(Q)) (left) and PDF (G(r)) for pure ceria (right) measured at various temperatures is shown here

The lattice parameters obtained from Rietveld and PDFgui refinements show that with increasing temperature that the lattice parameter increases whilst decreases as the sample is cooled. This can be due to either a thermal expansion or the reduction of Ce(IV) to Ce(III). Since the lattice parameter for the loaded samples does not return fully to the original value ~50^{o}C, it would suggest that the a majority of the cerium atoms oxidised back to Ce(IV) but not all leaving a slightly expanded unit cell. Note for HSA20 that hysteresis is evident whereas not seen for the Pd and Pt loaded samples.

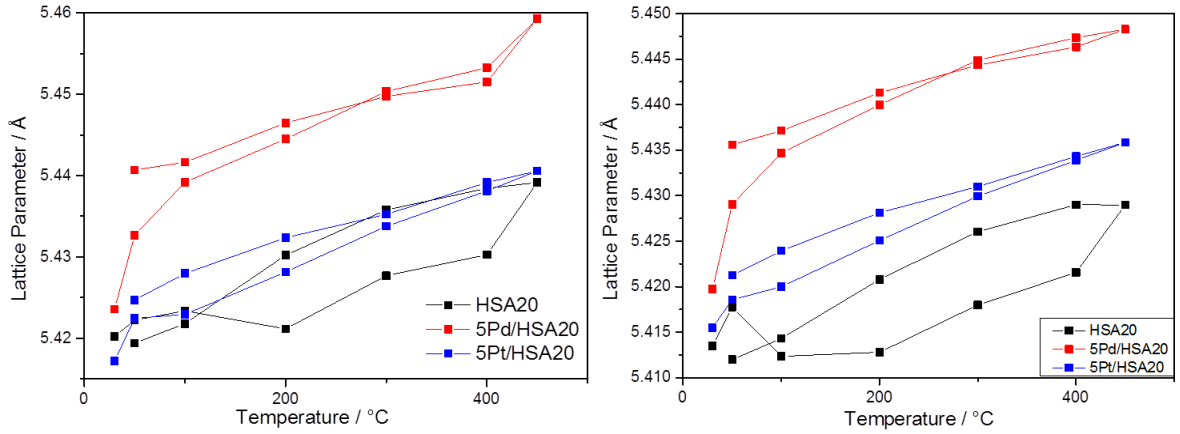

Figure 3: Lattice Parameter (a) / Å (Rietveld Refinement (left) PDFgui (right))

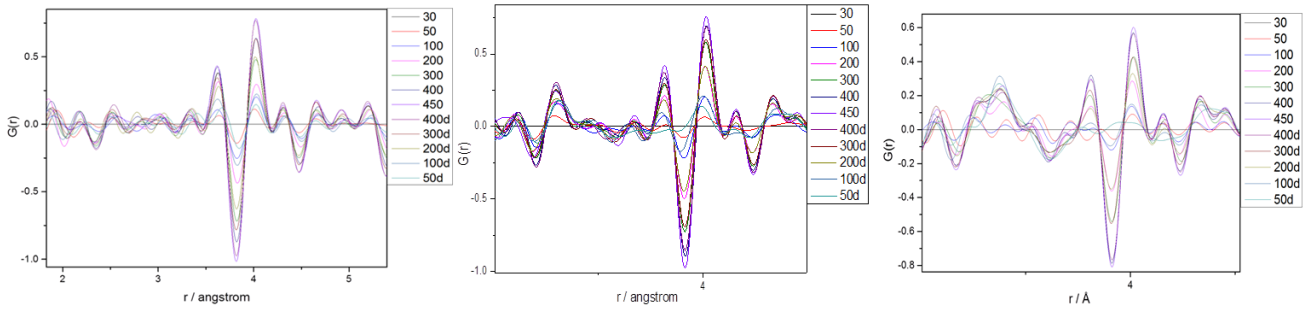

Figure4: G(r) differential curves for ceria (left), 5wt% Pd on ceria (middle) and 5wt% Pt on ceria (right)

This seems to make very little sense as the samples are being heated and cooled in hydrogen within a sealed system. This leads to the question of where is the oxygen coming from to reoxidise the Ce(III) atoms. A tentative explanation for the loss of oxygen during reaction (reduction) and oxidation back to Ce(IV) after cooling in hydrogen could be due to migration of oxygen from the original position to an interstitial or other defect sits at high temperature. As the sample is cooled these oxygen atoms are moving from the interstitial sites back to their 'perfect' sites within the crystal structure but as the surface oxygen atoms have been removed not all Ce(III) is completely oxidised.

In summary, the *in-situ* study of the samples show that there are differences between different metals loaded onto the samples. To further this work and investigate fully the movement of oxygen within the ceria lattice is to use neutron based total scattering technique to take advantage of the comparable scattering lengths of Ce and O. This data will be analysed along with X-ray data and the aim is to use reverse Monte Carlo methods to determine the structural model from these data sets.