Spectroscopic and Pair Distribution Evidence for Hexamethylenetetramine (HMT) as Adsorbents and Absorbents of Nano-ceria

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The size of nano-ceria particles can be controlled by the amount of time HMT and cerium nitrate are together in solution.[1] The interaction of HMT with cerium nitrate has been studied by in situ Small Angle Scattering (SAXS) and a core structure with a different surface structure is proposed.[2] The Diffuse Reflectance Fourier Transform Spectra (DRIFTS) of this nano-ceria shows significant adsorption of HMT on this surface that transforms to formate and finally carbonate during heating to 425 °C. The combination of PDF and DRIFTS analysis has been used to gain new insights into the structure of this nano-ceria.

A model of HMT interacting with the 111 surfaces of ceria can be made where H bonds from N in HMT can H-bond to OH groups on the ceria surface by aligning the 3-fold axes of the HMT and the 3-fold axis of the 111 surface of ceria (Figure 1). Examination of the G(r) of the Pair Distribution Function (PDF) does not show much evidence for this interaction because the scattering power of the light atoms in the HMT is too weak to show a significant signal when the heavy cerium atoms are present. However, signal enhancing techniques show some support for this model.[3]

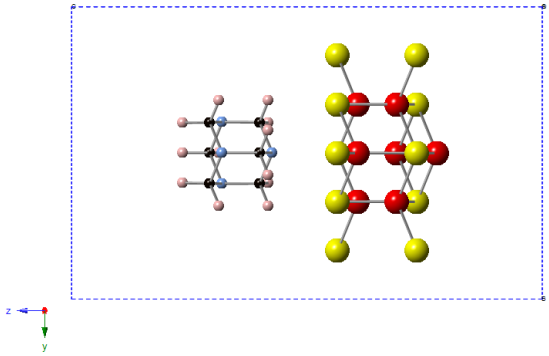

Figure 1. HMT adsorbed to ceria (C black N blue H pink) on Ceria Ce yellow O red)

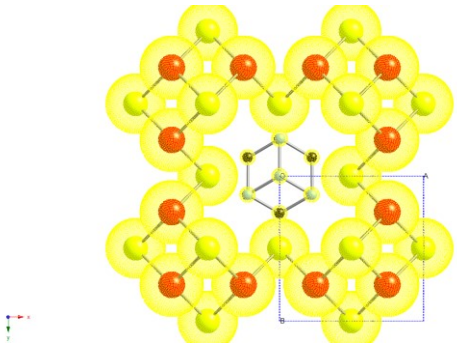

Figure 2. HMT absorbed in ceria. (Ce yellow O red)

The PDF analysis also suggests a Short-Range Order (SRO) phase in addition to a Long Range Order (LRO) phase that gives an improved fit. The SRO phase becomes smaller on heating and the LRO phase fraction increase with heating. Additional modeling shows that the SRO phase could also be interpreted as ceria with a CeO_8 fragment replaced with an HMT molecule (Figure 2).

The refinement of the temperature dependent PDF data shows the cell dimension variation found in the Rietveld refinement of the powder X-ray data. There is a spike in the cell dimension during the initial ramp which arises from the reduction of the ceria by the oxidation of the HMT or one of its decompaction products.

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