Understanding the mechanochemical synthesis of the perovskite $LaMnO_3$ and its catalytic properties

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[Abstract body]

Background

Mechanochemistry has gained attention as a viable way of producing catalysts for industrial processes; it offers a solvent free, low waste method of preparation, whilst also introducing additional active sites for catalysis, e.g. defects and oxygen vacancies. Catalytic performance is dependent on the phase composition, surface area and preparation method, all of which affects the properties of the final material. Mechanochemical grinding is known to form perovskites from their single metal oxide precursors, however, the use of grinding media and the formation of amorphous materials presents significant challenges when analysing the reaction and its resulting materials. We describe how XAS offers significant advantages over conventional characterisation techniques (e.g. XRD) for understanding the mechanochemical process and its influence on preparing $LaMnO_3$ for the decomposition of the environmental pollutant N_2O. Despite the extensive possible uses, commercial success for perovskite-type materials is yet to be achieved and highlights the need for development within the mechanochemical synthesis of perovskites.

Methods

Using a Planetary Ball Mill at 400 rpm with ZrO_2 grinding jars, Mn_2O_3 and La_2O_3 were added over YSZ grinding media. Milling time was 4 hours, with sampling every 30 min.
XAS measurements run at B18, DLS were performed at the Mn K-edge and La L_3-edge in transmission mode using QEXAFS setup with fast scanning Si(111) double crystal monochromator. XAS data processing was performed using IFEFFIT with the Horae package (Athena).

Results and Discussion

Characterising ‘time-slices’ through the milling process the XAS data provides a unique description of the action of mechanochemistry, which is not observed using other techniques (e.g. XRD, Raman, TEM, XPS). XRD studies run on milled samples show crystalline perovskite formed initially at 1 h of milling, with 100% of crystalline $LaMnO_3$ at 3 h. However, characterisation by XAS shows Mn-La scattering at the Mn K-edge is observed after 2 h of milling with La-Mn scattering at the La L_3-edge after 30 min of milling. We propose that after 30 min of milling the La precursor is dispersed over bulk Mn, with La-Mn scattering observed. After 2 h, enough energy has been supplied to break the bulk Mn and result in a chemical reaction to produce $LaMnO_3$ with Mn-La scattering observed. Initial catalytic testing by N_2O decomposition shows ball milled samples have better (3 h) and similar (4 h) behaviour to the that of the sol-gel prepared sample even though sol-gel has a surface area of 8 $m^2\ g^{-1,}$ compared to 5 $m^2\ g^{-1}$ of milled samples. By XRD, sol-gel and 3, 4 h ball mill samples show the same diffraction pattern, yet by XAS clear structural differences are observed, which could result in differences of catalytic activity.

Conclusion

Using XAS at both the Mn K-edge and La L_3-edge allows us to propose that La is first dispersed over bulk Mn, with perovskite formation occurring after enough energy has been supplied to break the Mn. XAS also provides a better understanding of the amorphous and distorted material produced via milling and will allow us better understand the properties of the final material.

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