Mixed FeO\textsubscript{x}-CeO\textsubscript{2-x} nanomaterials for chemical looping characterized by transmission electron microscopy and spatially resolved EELS

Turner S.\textsuperscript{1}, Meledina M.\textsuperscript{1}, Galvita V.\textsuperscript{2}, Poelman H.\textsuperscript{2}, Marin G. B.\textsuperscript{2}, Van Tendeloo G.\textsuperscript{1}

\textsuperscript{1}EMAT, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium, \textsuperscript{2}Laboratory for Chemical Technology, Ghent University, Technologiepark 914, 9052 Ghent, Belgium

Email of the presenting author: stuart.turner@uantwerpen.be

Mixed FeO\textsubscript{x}-CeO\textsubscript{2-x} nanomaterials are promising candidates for use as oxygen storage materials in the production of H\textsubscript{2} by chemical looping. The technology of chemical looping is based on periodic reduction/re-oxidation cycles of metal oxides, designed to convert hydrocarbons to hydrogen with a quality that exceeds the requirements of all types of fuel cells.\textsuperscript{1,2} In this work, a series of mixed FeO\textsubscript{x}-CeO\textsubscript{2-x} with varying Fe/Ce content are characterized using a combination of advanced imaging techniques and spatially resolved EELS, in order to characterize the presence and nature of the constituting components. The oxide materials are studied throughout the oxidation/reduction cycle, paying special attention the morphology and surface features of the FeO\textsubscript{x}/CeO\textsubscript{2-x} material.

Low iron content materials (e.g. 5wt.\% FeO\textsubscript{x}/CeO\textsubscript{2-x}) typically consist of ceria nanoparticles with sizes ranging from approximately 20 to 60 nm. Electron diffraction and imaging show no evidence for the presence of a separate Fe\textsubscript{2}O\textsubscript{3} (or FeO\textsubscript{x}) phase in this material. The ceria nanoparticles do show the presence of nanometer-sized voids, which have previously been observed in nanosized ceria. Spatially resolved EELS maps show that both voids and ceria surfaces are decorated with isolated Fe atoms, and that the surface atoms of the ceria nanoparticles and the voids are in a reduced state compared to bulk CeO\textsubscript{2}.\textsuperscript{3} Particular attention has been paid to possible changes in the oxidation state and clustering of these Fe species upon oxidation and reduction. The high iron content materials consist of α-Fe\textsubscript{2}O\textsubscript{3} nanoparticles decorated by significantly smaller ceria nanoparticles. In these samples, both structural and valency changes at the FeO\textsubscript{x}/CeO\textsubscript{2-x} interface upon cycling have been studied in detail.

1) V. Galvita et al., Topics in Catalysis 2011, 54, 907.
2) V. Galvita et al., Ind. Eng. Chem. Res. 2013, 52, 8416
3) S. Turner et al. Nanoscale, 2011, 3, 3385

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Fig. 1: (a) Overview HAADF-STEM image of a 5wt.% FeO$_x$–CeO$_{2-x}$ sample. (b) HR-HAADF-STEM showing strong faceting and the presence of voids. (c) Overview HAADF-STEM image and corresponding EELS maps: the Fe is enriched at the ceria surface and within the voids.

Fig. 2: (a) High resolution EELS references for Ce$^{4+}$ and Ce$^{3+}$. (b) Overview HAADF-STEM image and (c) Ce$^{3+}$/Ce$^{4+}$ map showing surface reduction in the ceria nanoparticles. (d) HAADF-STEM image of the surface of a ceria nanoparticle with (e) corresponding EELS spectra from the surface (black spectrum) and near-surface (blue spectrum) regions.