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7	D7.2	Synthesis of nanostructured oxygen carrier materials in a ceramic matrix	Julian Tolchard Paul Inge Dahl	1	SINTEF	R	PU	30.06.2016	27.06.2016

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1 Introduction

Based on the NanoSIM WP3 study, iron oxide was chosen as the oxygen carrier material to be utilised within WP7 to demonstrate the effect of nanostructuring on CLR performance. Fe₂O₃ has suitable thermodynamic properties, is environmentally benign and there is better availability of phase relation data relative to other candidate materials such as Mn₂O₃, which simplifies the search for candidate support/matrix materials.

Kinetic studies of unsupported iron nanoparticles have revealed improved reactivity, reduced mass resistance and enhanced heat transfer [1]. However at temperatures above 450 °C particle sintering results in coarsening of the particles (up to µm scale), and the observed benefits disappear. In order to utilize the nanostructured materials it is therefore necessary to endow them with much greater thermal stability. This can be achieved by dispersing the active nano-catalyst within an inert support material, which suppresses coarsening and sintering via physical separation [2, 3]. In effect, a "mechanical caging" mechanism stabilises the nanoparticles in the mesopores of the support material [4]. Such stabilized nano-composites have been successfully synthesised through reverse emulsion processes [5-7], but these routes are neither cost efficient, environmentally friendly, nor viable for large scale production. More cost effective and "green" synthesis routes are therefore sought within the NanoSim project.

The current literature on nanostructured oxygen carrier materials focuses on oxides of first-row transition metals, which are then dispersed onto a thermally stabilizing amorphous barium hexaaluminate (BHA) support [2, 3, 5, 6, 8, 9]. BHA as the support material has a high sintering temperature and low reactivity towards metal oxides under employed operating conditions. Substitution of BHA due to cost and in some cases toxicity of Ba-precursors, is desirable however. The current report will focus on work obtained with lanthanum silicate as an alternative matrix material.

The need to synthesise supports in-house stems from the limitations of commercially available fluidizable support materials: These are typically mesoporous (2-50 nm) alumina or aluminosilicate materials, designed for catalyst deposition via solution impregnation, and so demonstrate an average pore diameter below or up to 10 nm. This makes impregnation of dispersed nanoparticles difficult or impossible. As WP7 seeks to demonstrate size dependent properties, controlled nanoparticle synthesis ex-situ from the support is necessary. That said, it is also a goal within NanoSim to evaluate a relatively large sample (10's of grams) of porous fluidizable particles (uniform spherical particles in the size range of 100-200 µm) containing sufficient active nanostructured oxygen carrier material (iron oxide).

A two-pronged approach is then presented in this report, with nanostructured oxygen carrier materials produced and tested on two different scales:

- 1) Small scale (5-10 gram batches) synthesis of iron oxide nanoparticles embedded in a highly porous lanthanum silicate matrix material
- 2) Large scale (kg) wet impregnation of commercially available, mesoporous, fluidizable alumina support particles, with iron oxide, from aqueous iron nitrate solution.

The small scale batches will be applied for investigating the effects of particle size on reforming reactions in micro-reactor tests in relevant conditions, while the larger scale batches will be used for a lab-scale pilot reactor operating at elevated pressures.

2 Preparation of nanostructured oxygen carriers

2.1 Iron oxide nanoparticles embedded in lanthanum silicate matrix

Two types of iron oxide nanoparticles are being embedded into lanthanum silicate based matrix material;

- 1) Commercially available, irregular shaped (10x50-100 nm) nanoparticles. These were purchased from Sigma Aldrich in the form of a water-based dispersion. The product number is 720704.
- 2) Finer (<10 nm), regular shaped (spherical) iron oxide nanoparticles are synthesized through in-house methods. Again, these were utilised in the form of a water based dispersion, and produced according to the method of Zhang et. al. [10]

From imaging with a scanning electron microscope (SEM) the larger nanoparticles are highly asymmetric rods as shown in Figure 1, while the finer, synthesized nanoparticles shown in Figure 2 are spherical. The corresponding size distribution for the smaller, in-house synthesized particles is given in Figure 3. This was calculated via image analysis of transmission electron micrographs.

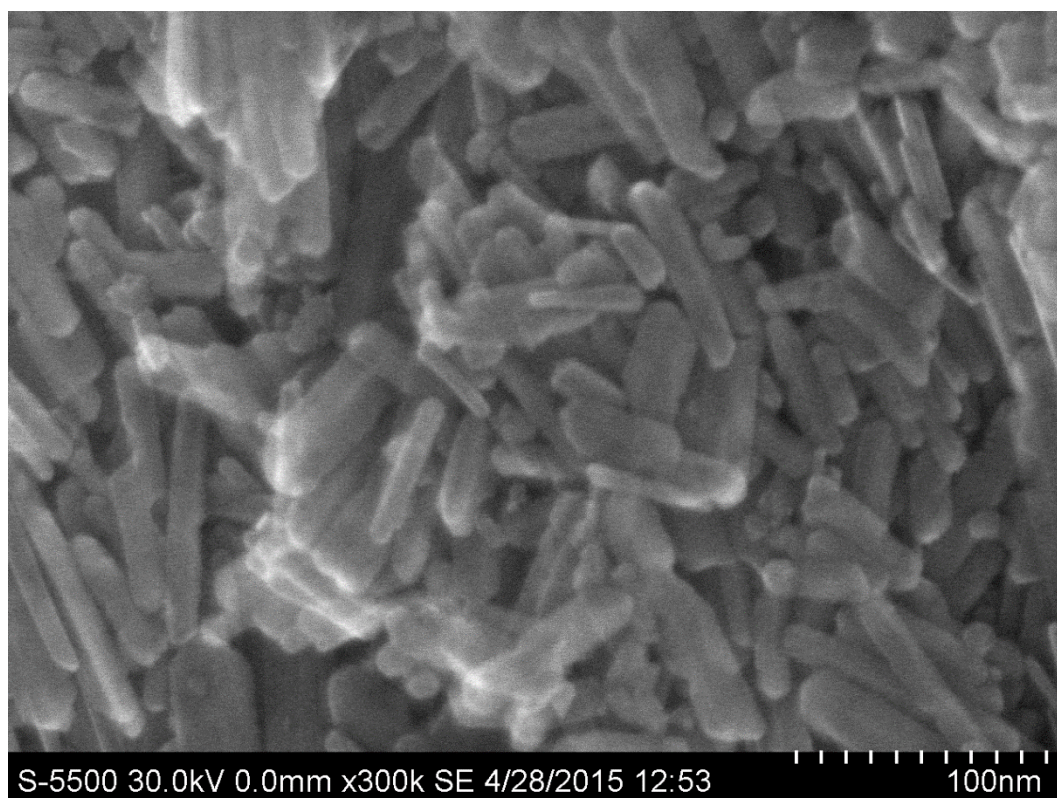


Figure 1: Iron oxide particles as purchased from Sigma Aldrich

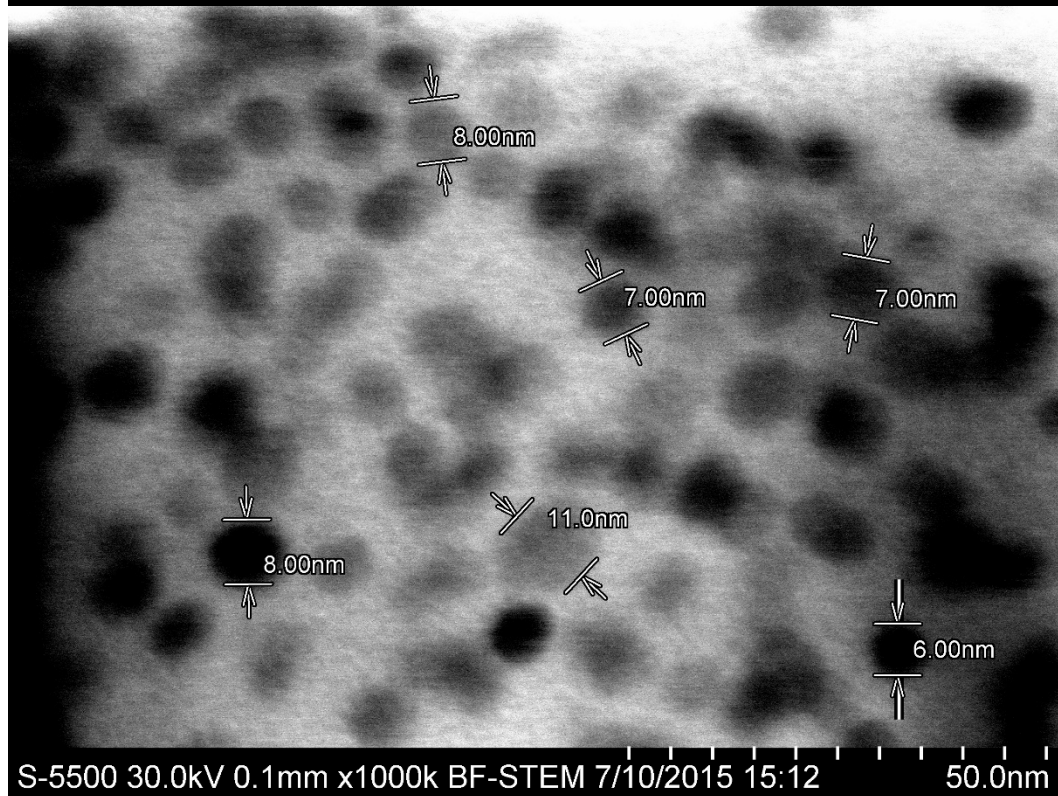
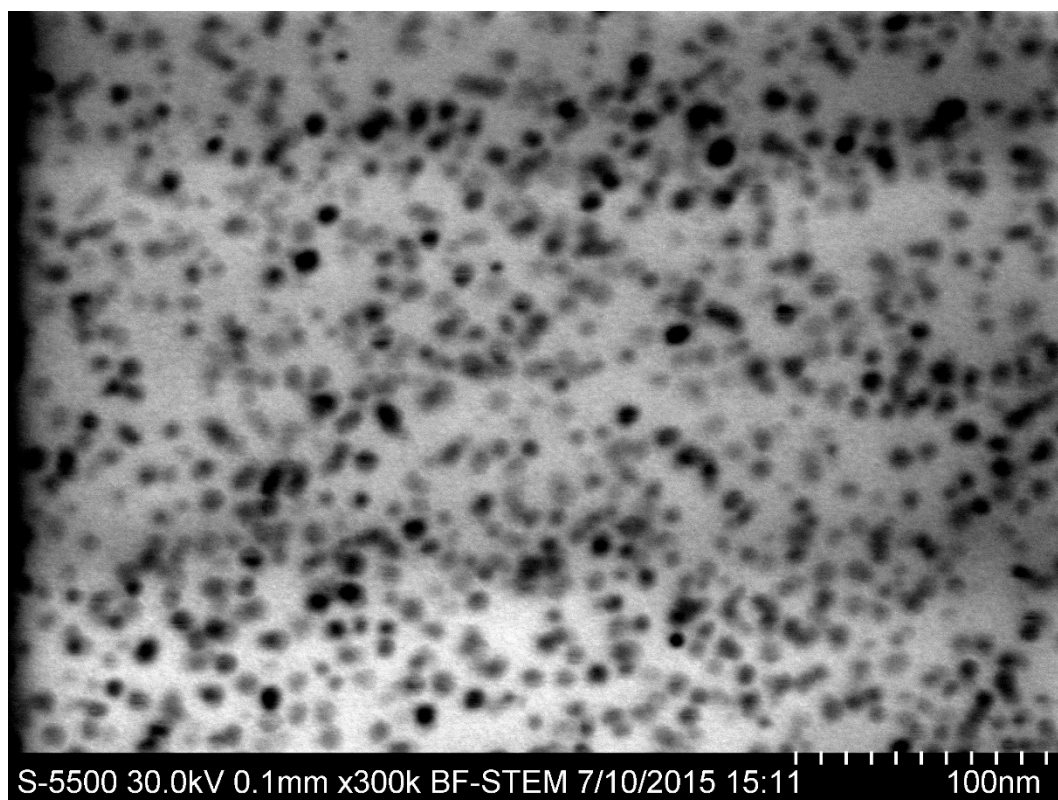


Figure 2: STEM images of in-house synthesized iron oxide nanoparticles.

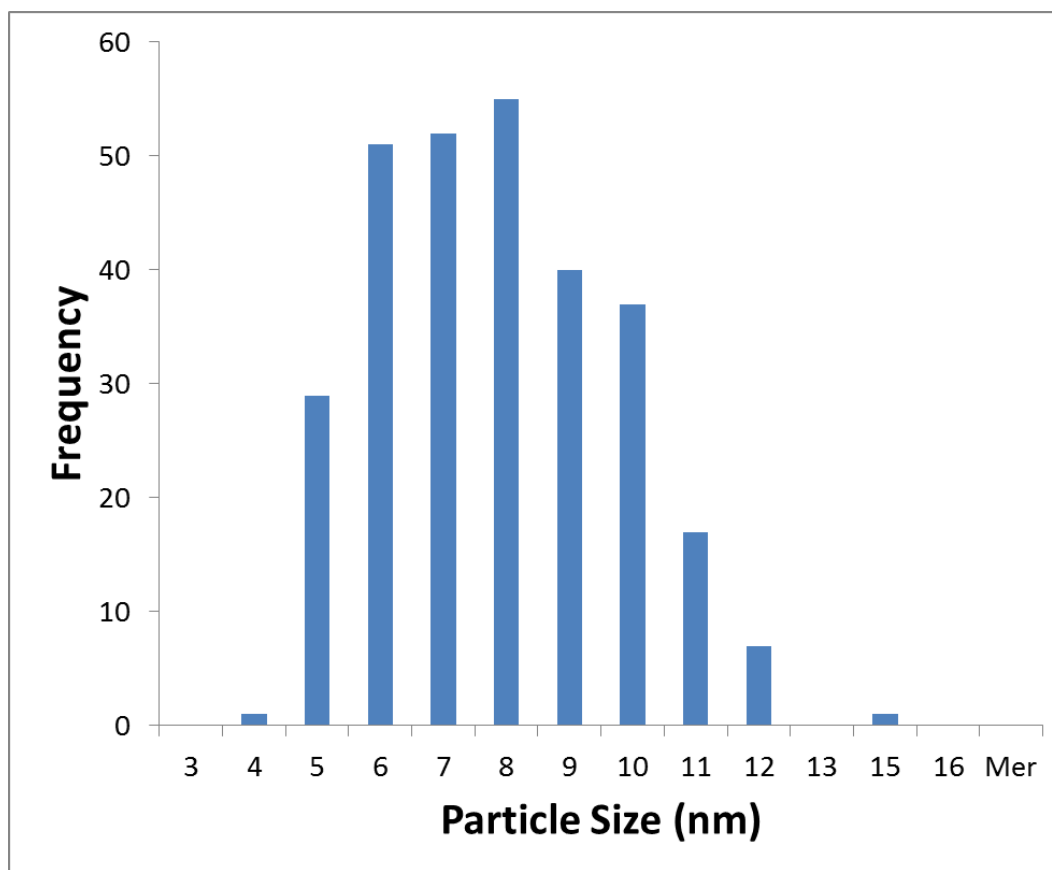


Figure 3: Size distribution of synthesized iron oxide nanoparticles.

The nanoparticles were supported on a matrix of Lanthanum Silicate ($\text{La}_{9.33}\text{Si}_6\text{O}_{26}$) synthesised via a modification of the sol gel method reported by Vojisavljevic et.al. [11]. In short, precursors of Lanthanum acetate and Tetraethylorthosilicate (TEOS) are reacted together to form a gel, which is then dried and heat-treated to form the final product. Ideally, the water dispersed nanoparticles are mixed into the precursor solution prior to gelling, but all reported sol-gel routes for $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ synthesis involve acid catalysis, and thus very low pH. The lanthanum precursor also becomes insoluble at around pH 5 and above. As Fe_2O_3 becomes soluble below pH~5, it was not possible to disperse the nanoparticles prior to gelling. A modification in which the pH was kept at around 5 was attempted, with gelling promoted via addition of excess ammonia. This is not ideal though, as it is very difficult to balance the solubilities of the lanthanum precursor and Fe_2O_3 during mixing, and as the Lanthanum becomes insoluble at higher pH, there is precipitation before gelling and thus formation of undesired phases in the product. This route was used for the sample synthesised using the larger nanoparticles acquired from Sigma Aldrich though. For the smaller, in-house prepared nanoparticles, the support was synthesised via the acid catalysed reaction, fired at 400 °C and then the nanoparticles were mixed in manually using a pestle and mortar. No attempt to gel a solution with these nanoparticles was made due to fears that their smaller size would make them very soluble in the event that the solution pH drifted too low.

A secondary electron micrograph of the sample synthesised using in-house synthesised Fe₂O₃ is given in Figure 4. Due to the particle size and poor backscatter contrast, distinguishing between the LS support and the nanoparticles is difficult using the available BSE-SEM/EDS equipment. Well distributed spherical nanoparticles (~6 nm) are observed to be dispersed on larger particles, and as these correlate extremely well with the as-synthesised Fe₂O₃ it is interpreted that these are the particles seen. EDS measurement over a large area of this sample gives a loading of approx.. 5wt% Fe₂O₃, compared to a higher loading of ~20 wt% for the sample synthesised using Sigma Aldrich Fe₂O₃.

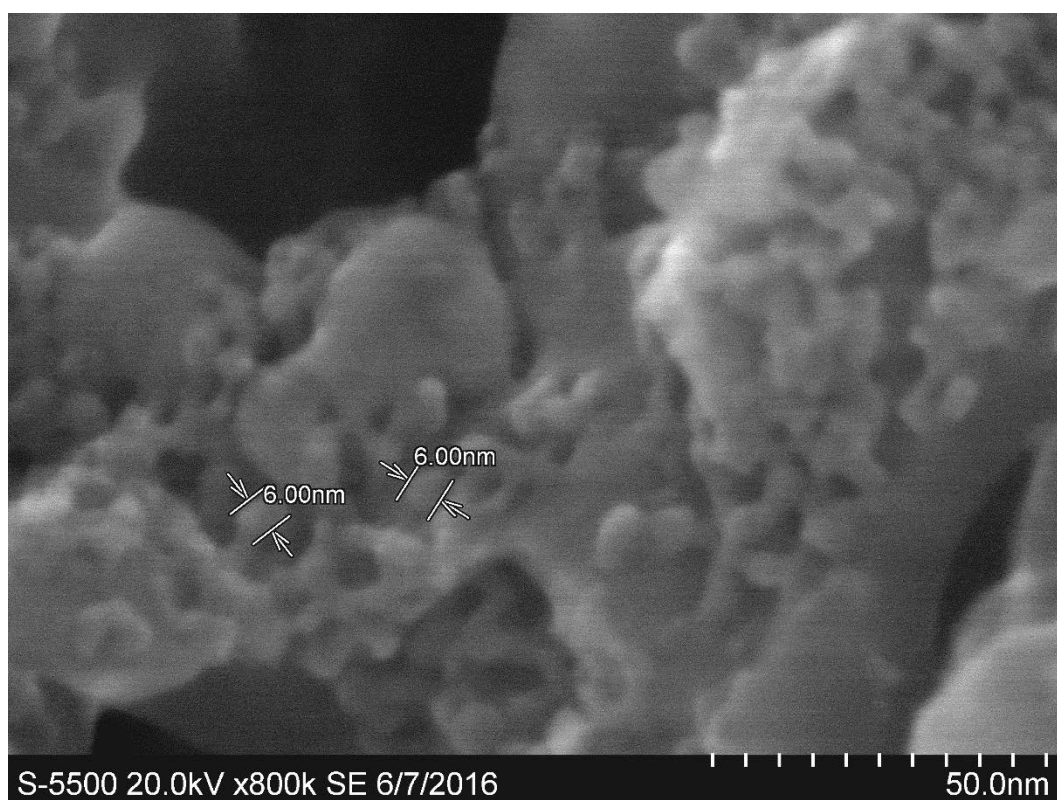


Figure 4: Iron oxide nanoparticles onto lanthanum silicate support material.

2.2 Spherical alumina supports with iron oxide from wet impregnation)

Gamma-alumina supports from Saint-Gobain were impregnated via the incipient wetness method using saturated aqueous iron nitrate solution, followed by calcination at 400°C for 6 hours in ambient air. Based on mass change, a loading of 12 wt% iron oxide (hematite, Fe₂O₃) was obtained. The particle size distribution of the bare and impregnated supports are presented in Figure 5. After sieving the impregnated particles (>100 μm, <250 μm) a distribution not far from the bare supports was obtained, however, a tendency to agglomeration is seen and some finer particles (<100 μm) remains. The heat treated particles are also depicted in Figure 6.

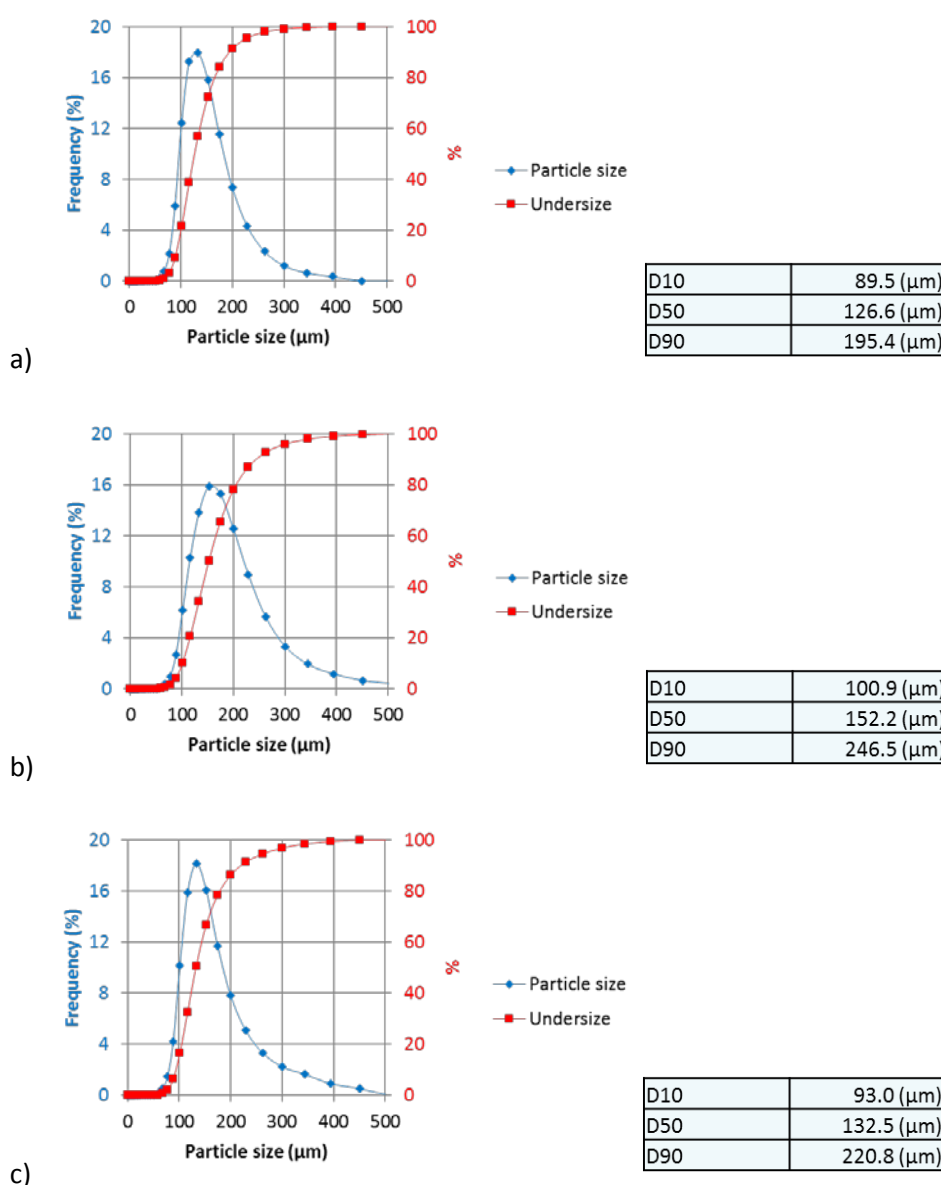


Figure 5: Particle size distribution curves with corresponding values for D10, D50 and D90 for bare alumina supports (a) and alumina supports with iron oxide before (b) and after (c) sieving <100 μm, 250 μm>.

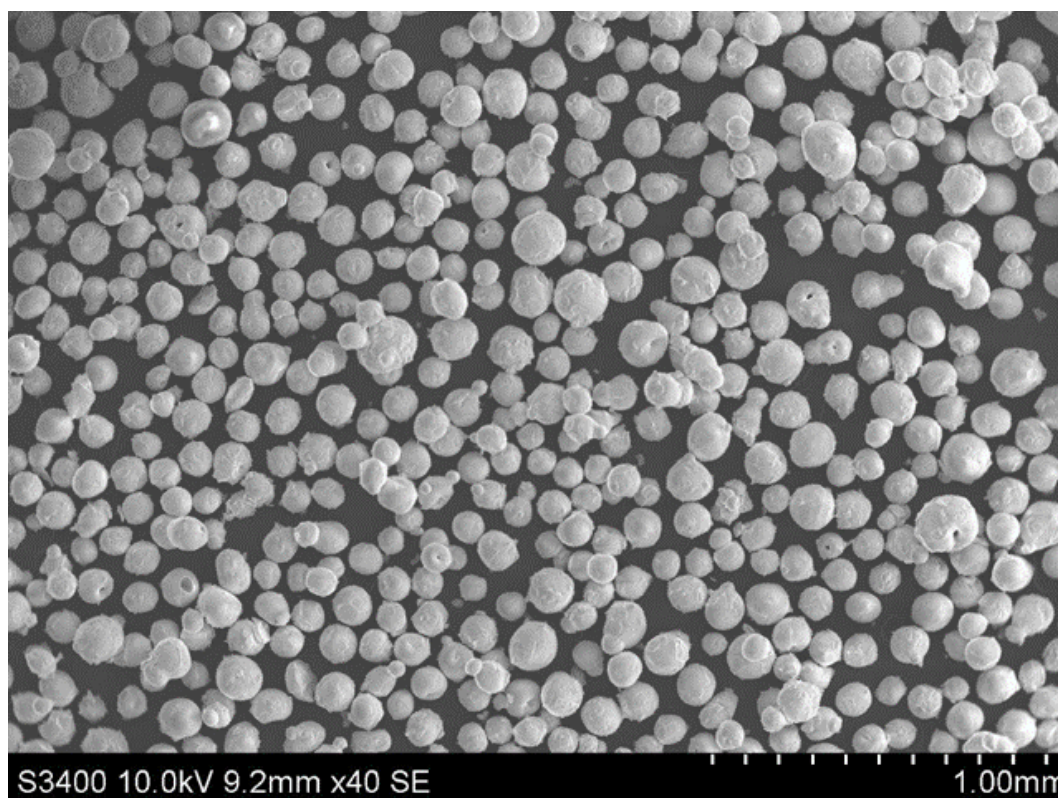


Figure 6: Scanning electron microscopy (SEM) image of alumina supports impregnated with iron oxide.

As shown in Table 1 the BET surface area and total pore area of the support was decreased from the impregnation, whereas the pore diameter was not reduced. This could be an indication of poor impregnation and surface coating of the supports. This was confirmed by SEM/EDS analysis as shown in Figure 7. Further work is hence required for optimization of the impregnation procedures.

Table 1: BET surface area from nitrogen adsorption/desorption measurements and pore area/size from mercury intrusion measurements for bare and impregnated alumina supports.

	Bare support	Impregnated support
BET surface area (m ² /g)	153	143
Total pore area (m ² /g)	191	159
Median pore diameter (Area) (nm)	9.3	9.2
Average pore diameter (4V/A) (nm)	20.4	23.9

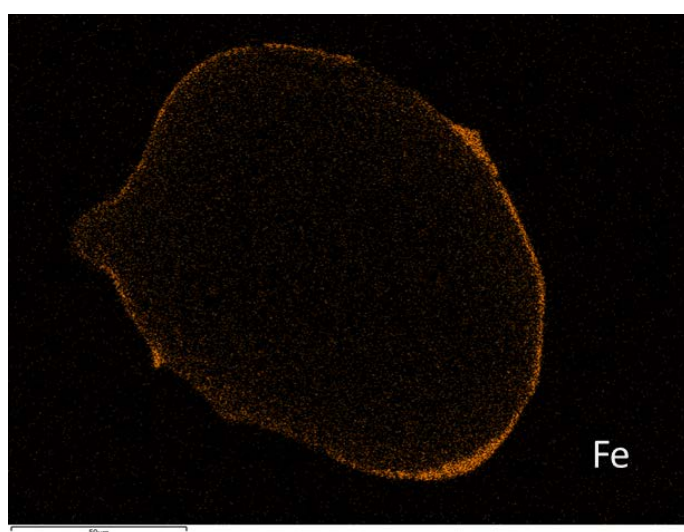
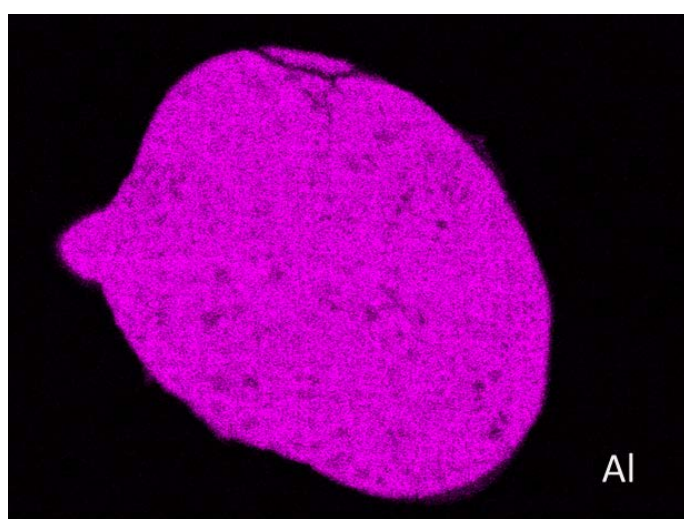
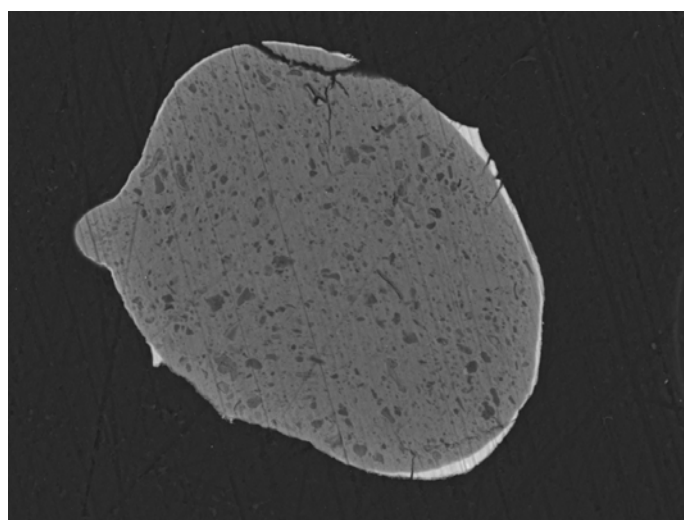


Figure 7: Cross-section SEM/EDS analysis of impregnated alumina particle.

3 Material thermochemical stability

The as-synthesized materials were subjected to thermal treatment at different temperatures in ambient air, and subsequent evaluation of phase formation through X-ray diffraction studies (XRD) in order to investigate the thermochemical stability as well as coarsening of the nanoparticles.

For the iron oxide particles embedded in lanthanum silicate, the success of the method is demonstrated in figure 8, which shows that the in-house synthesised (<10nm) nanoparticles on La_{9.33}Si₆O₂₆ were not seen to form any secondary phases or exhibit any sort of increase in crystallinity after firing at 700 °C for 6 hours.

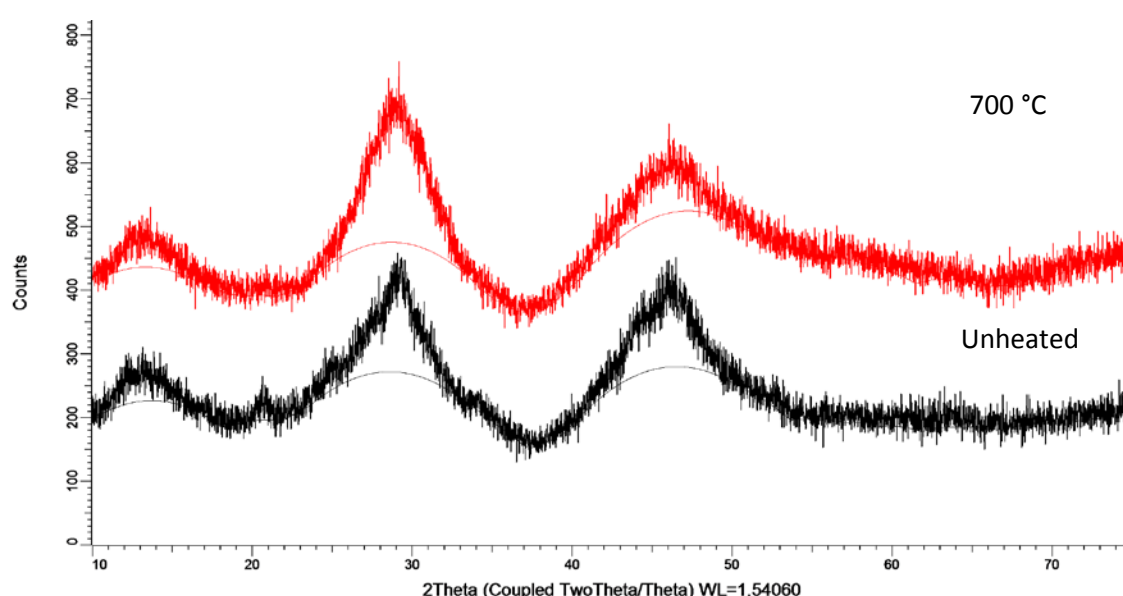


Figure 8: XRD of the in-house prepared (<10nm) Fe₂O₃ supported on La_{9.33}Si₆O₂₆, before and after heat-treatment in air at 700 °C.

For the impregnated alumina particles the fitted XRD data (Figure 9) indicate a reduction in the unit cell parameters as compared to the reference hematite, Fe₂O₃, structure – see Table 2. This agrees well with thermodynamics and a certain degree of solid solution of alumina in the hematite structure. Based on the work of Schwertmann et al. [10], as presented in Figure 10, the unit cell parameter *a*, indicates a substitution of 5-10 % of the Fe in hematite with Al for the impregnated alumina sample after heat treatment at 400°C. This substitution is increased with heat treatment at elevated temperature. Such substitution may not be crucial for the properties of the active (iron oxide) material, however it will for sure be affected and hence operation at lower temperatures (<800°C) is advised.

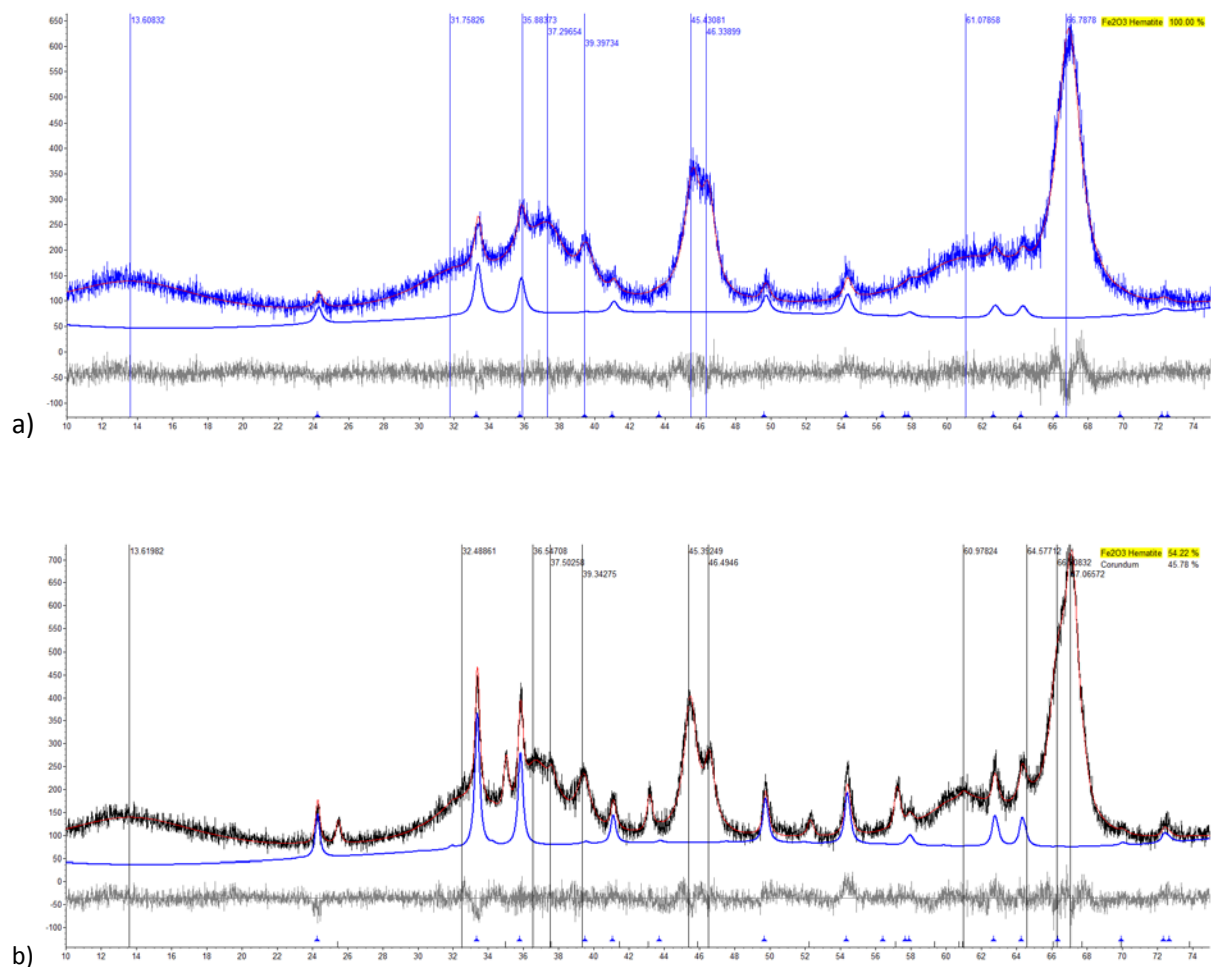


Figure 9: XRD fitted data for alumina supports impregnated with iron oxide after heat treatment at a) 400°C and b) 800°C for 6 hours in ambient air.

Table 2: Unit cell parameters obtained from fitted XRD data of impregnated alumina after heat treatment at 400 and 800°C for 6 hours in ambient air.

Unit cell	a (Å)	c (Å)
400°C	5.022	13.705
800°C	5.016	13.682
Reference, Fe ₂ O ₃	5.035	13.753

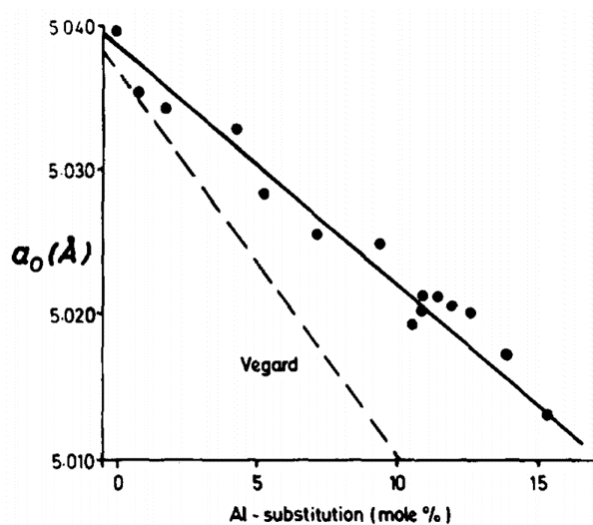


Figure 10 Al-substitution of hematite (Fe_2O_3) as reported by Schwertmann et al. [12]

From SEM analysis of impregnated alumina particles heat treated at 800°C, see Figure 11, it is evident that the impregnation needs improvements as there appears to be a thick surface coating of the particles which cracks. This is expected to cause significant unwanted fines in a fluidized bed reactor.

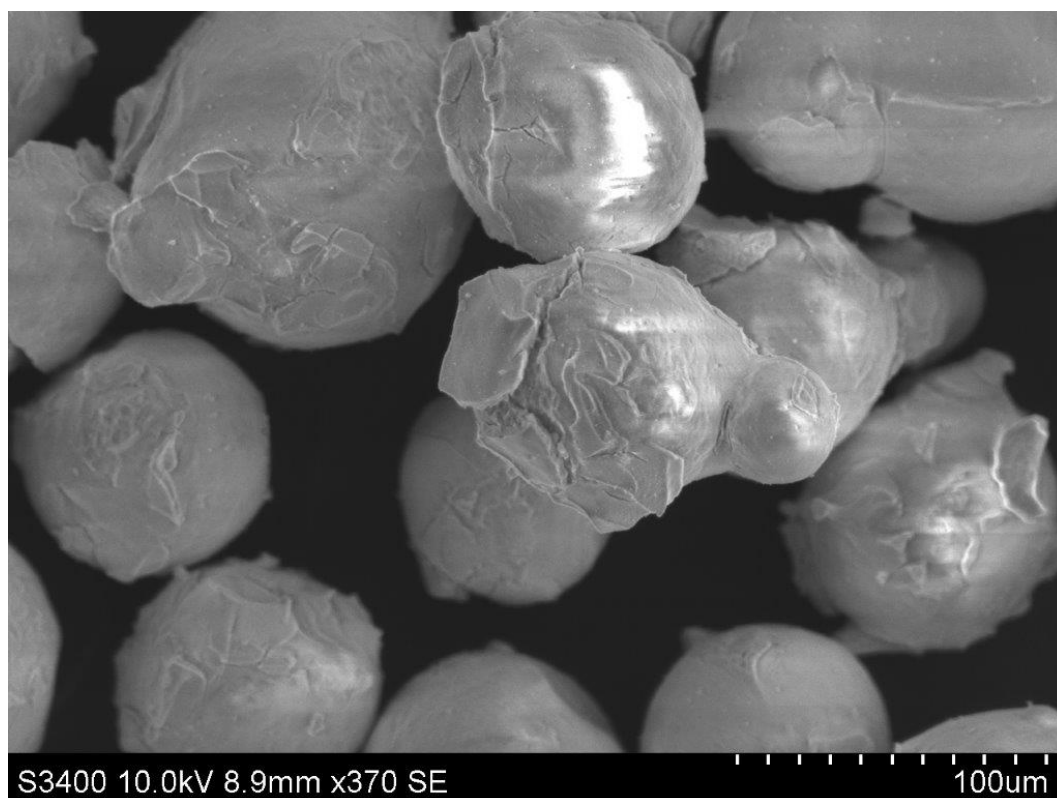


Figure 11: Porous alumina spheres impregnated with iron oxide (from nitrate solution) after heat treatment at 800°C for 6 hours in ambient air.

4 Summary

Synthesis of several 10 gram batches of nanostructured oxygen carriers embedded in lanthanum silicate matrix material have been realized using irregular, rod shaped particles as well as smaller (<10 nm), regular shaped particles of iron oxide. The materials have been characterized and the results indicate that the nanostructures remain up to 700°C.

On a larger scale (kg) an iron oxide loading of 12-13 wt% in commercially available, porous alumina spheres was obtained by wet impregnation with iron nitrate solution and subsequent heat treatment. The process is still to be optimized to reduce the surface coating of the alumina particles in order to minimize the generation of fines, expected from fluidization of the particles at high temperatures (> 800°C).

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