Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Local environment of Fe dopants in Nanoscale Fe:CeO_{2-x} oxygen storage material.

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S1. XRD analysis

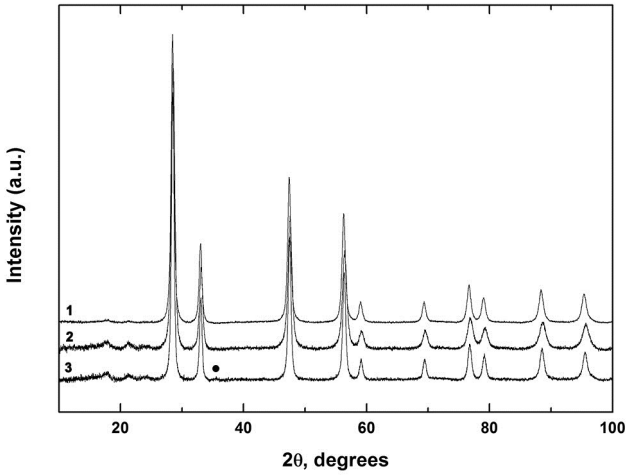

Fig. S1. XRD patterns of the undoped ceria (1), 5wt.% Fe: CeO_{2-x} (2) and 5wt.% Fe: CeO_{2-x} after ten cycles (3) samples. The black circle indicates the position of the (110) α-Fe_2O_3 peak.

Sample name	Cell parameter, Å
Undoped CeO_{2-x}	5.4088(4)
5 wt.% Fe:CeO_{2-x}	5.3974(5)
5 wt % Fe:CeO_{2-x} after 10 redox cycles	5.4019(4)

Table S1. Cell parameters, calculated by the least squares method from the XRD patterns acquired from undoped ceria, 5wt.% Fe: CeO_{2-x} and 5wt.% Fe: CeO_{2-x} cycled samples.

S2. XPS analysis of as prepared Fe:CeO_{2-x}

XPS was performed on Fe:CeO_{2-x}, as requested. The Fe2p signal was not useable as it covered with Auger peaks from Ce (CeMNN) (figure S2a). Therefore, the weaker signal of Fe3p was investigated, following an analysis of Yamachita[1](figure S2b). Based on literature, the position of this photoline is at binding energy 55.5 eV for Fe^{3+}, while it shifts down to 53-54 eV for

Fe^{2+}.[2,3] Curve fitting of the Fe3p photoline showed that the main contribution originates from Fe^{2+}, with a minor signal from Fe^{3+}, 86 vs. 14%, respectively.

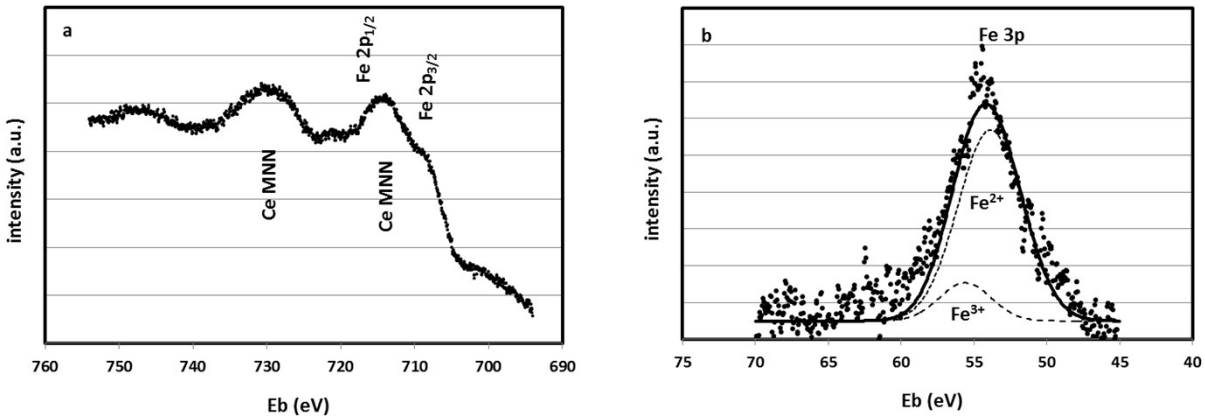

Figure S2: *XPS on Fe:CeO_{2-x}* a: Auger emission lines of Ce MNN, overlapping the photoemission lines of Fe2p; b: Fe3p photoemission line with curve fitting of Fe^{2+} (dotted line) and Fe^{3+} (dashed line) contribution; sum of fitting contributions (full line).

S3. TEM analysis after a half redox cycle

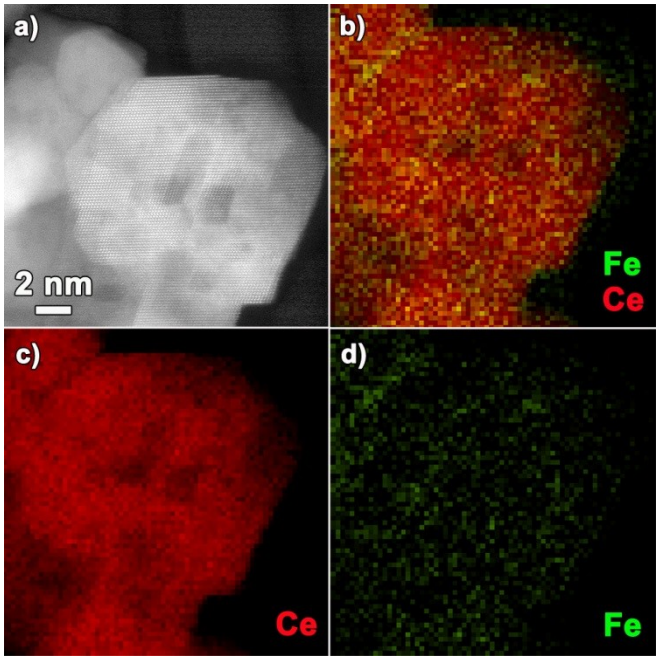

Fig. S3 *Fe:CeO_{2-x} after a half redox cycle (in reduced state)*; a) HAADF-STEM image showing the mapped ceria nanoparticle together with b) color overlay of the Ce and Fe, c) Ce, f) Fe EELS maps.

S4. TEM analysis after one hundred redox cycles

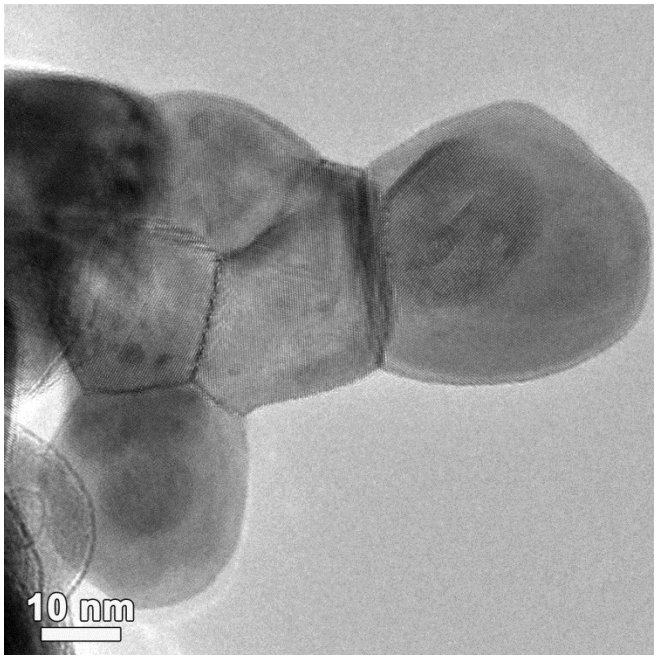

Fig. S4 *Fe:CeO_{2-x} after one hundred redox cycles;* HRTEM image of sintered ceria nanoparticles.

References

1. T. Yamashita, P. Hayes, *Appl. Surf. Sci.*, 2008, 254, 2441–2449.
2. A. Mekki, M. Salim, *J. Electron. Spectrosc. Relat. Phenom.,* 1999, 101–103, 227–232.
3. J .Knudsen, L.R. Merte, L.C. Grabow, F.M. Eichhorn, S. Porsgaard, H. Zeuthen, R.T. Vang, E. Lægsgaard, M. Mavrikakis, F. Besenbacher, *Surf. Sci.*, 2010, 604, 11–20.