Stabilization of CeO_2 nanoparticles in a CO_2 rich solvent†

**Martin J. Hollamby,[a] Kieran Trickett,[a] Ana Vesperinas,[a] Carl Rivett,[b]
David C. Steytler,[b] Zoe Schnepp,[a] Jon Jones,[a] Richard K. Heenan,[c]
Robert M. Richardson,[a] Otto Glatter[d] and Julian Eastoe*[a]**

Received (in Cambridge, UK) 8th July 2008, Accepted 4th August 2008
First published as an Advance Article on the web 29th September 2008
DOI: 10.1039/b811563j

Here it is shown that the chemical nature of outer organic surfactant layers, used to stabilize inorganic nanoparticles (NPs), is a key factor controlling solubility in a mixed liquid CO_2—heptane (10% vol) solvent.

Ceria (CeO_2) NPs have been prepared from water-in-heptane (w/o) microemulsions stabilized by two different surfactants: a recognized CO_2-phobe (AOT, sodium bis-(2-ethylhexyl)sulfosuccinate) and a known CO_2-phile (TC14, sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulfonate), both shown in Fig. 1a and b insets. Extensive characterization indicates that these nano-ceria cores are essentially the same size and structure, hence they represent convenient model particles. When added to the CO_2–heptane solvent, AOT-coated NPs exhibit negligible solubility whereas the TC14-coated NPs can be dispersed in the CO_2 phase. The novel aspect here is that variation of the outer organic stabilizing layers has been explored in isolation.

CeO_2 or CeO_2-containing mixed metal/metal oxide NPs are known catalysts for oxidation reactions.[1–4] Microemulsion-templated synthesis[5] has been previously applied to synthesize fine dispersions of such materials.[6–8] The resulting NPs are surfactant-coated, allowing re-dispersion in different solvent media. A commonly employed surfactant for this purpose is AOT.[5,9]

Dispersion of NPs in green solvents, such as supercritical CO_2 (sc-CO_2), is a major challenge. The potential benefits of employing sc-CO_2 as replacement solvent for a variety of industrial processes (in particular heterogeneous catalysis) are well documented.[10] Unfortunately sc-CO_2 is a very poor solvent and specialist surfactants are required to solubilize most polar materials.[11] The microemulsion route has previously been used to synthesize NPs in sc-CO_2,[5] typically employing fluorocarbon (FC)-based amphiphiles. Catalysis of hydrogenation reactions by FC-stabilized Pd and Rh NPs in sc-CO_2 has also been described.[12]

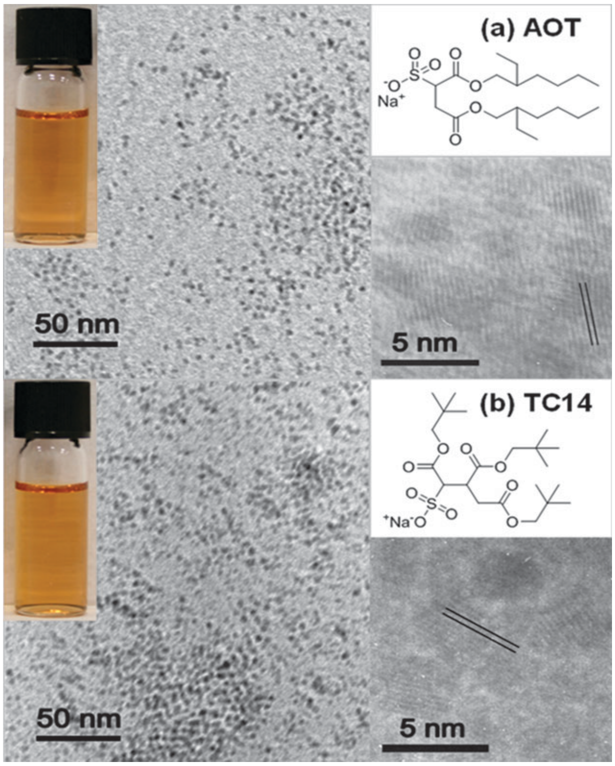

Fig. 1 (Insets top left) Photographs of (a) AOT-coated and (b) TC14-coated CeO_2 NP dispersions; (inset top right) chemical structures of (a) AOT and (b) TC14; (inset bottom right) HRTEMs of (a) AOT-coated CeO_2 NPs showing fringes corresponding to a lattice separation of 2.7 ± 0.3 Å and (b) TC14-coated CeO_2 NPs with lattice separation = 2.8 ± 0.4 Å; (main figures) TEM images of (a) AOT- and (b) TC14-coated CeO_2 NPs.

However, FCs are both expensive to source and environmentally persistent, so clearly lower-cost hydrocarbon (HC)-based amphiphiles would be preferable. There has been some success: silver nanoparticles have been synthesized and stabilized in sc-CO_2.[13] Whilst these studies represent groundbreaking work, the systems used are quite complex, with more than one surface-active component. Recently, super CO_2-soluble tri-chain AOT-analogue surfactants have been reported: of these TC14 (Fig. 1) is the most promising.[14] Moreover, tri-chain surfactants have been shown to efficiently stabilize w/o microemulsions at room temperature and pressure.[15,16] Advantages of TC14 over previously studied stabilizers[5,12,13] are that it is both HC-based and a clean, single component surfactant.

---

[a] *University of Bristol, Cantock's Close, Bristol, UK BS8 1TS. E-mail: Julian.Eastoe@bristol.ac.uk; Fax: +44 (0)117 925 1295; Tel: +44 (0)117 928 9180*
[b] *University of East Anglia, Norwich, UK NR4 7TJ*
[c] *ISIS Pulsed Neutron and Muon Source, Rutherford Appleton Laboratories, Chilton, Didcot, UK OX11 0QX*
[d] *Karl-Franzens Universität Graz, 8010 Graz, Austria*

† Electronic supplementary information (ESI) available: Particle size analysis, experimental details, SAED analysis, UV spectra not shown in main paper, fitted SANS profiles, details of model fits used. See DOI: 10.1039/b811563j

Table 1 Comparison of AOT- and TC14-stabilised microemulsion (ME) droplet diameters (SANS) with corresponding surfactant-coated NP diameters (SAXS and TEM)

Stabilizing layer	D_{ME}/nm (SANS)	D_{NP}/nm (SAXS)	D_{NP}/nm (TEM)
AOT	2.8 ± 0.3	3.1 ± 0.3	3.5 ± 0.4
TC14	2.8 ± 0.3	3.2 ± 0.4	2.6 ± 0.3

The prepared NP dispersions are straw colored and optically transparent (Fig. 1). Transmission electron microscope (TEM) images (Fig. 1) show NPs to be spherical and polydisperse. The average NP diameter† (Table 1) is found to be of the order of 3 nm for both samples, in agreement with previous work (AOT-coated).[6] High resolution (HR) TEM coupled with selected area electron diffraction (SAED) has been employed to study the crystalline nature of the nanoparticles. Lattice separations (HRTEM image) and *d*-spacings (SAED) obtained are consistent with a fluorite crystal structure of CeO_2.† UV-Vis spectra show elevated absorbance in the region 300–400 nm, consistent with formation/stabilization of CeO_2 NPs.† To further characterize NP dispersions in heptane, small-angle X-ray scattering (SAXS) was used† (Fig. 2). Modelling the data with a particle form factor for a Schultz distribution of polydisperse spheres yielded average NP diameters (Table 1). Diameters for the water droplets of initial w/o microemulsions obtained by fitting small-angle neutron scattering data† are also summarized in Table 1. Particles prepared by microemulsion-templated synthesis are often larger than precursor reactant-containing droplets[5] as seen here. SAXS diameters found for the NPs ($\sim$3 nm) agree well with values from TEM.

Before testing CO_2 solubility, samples were first dried to remove heptane. Initially, pressure-induced cloud points[11] (P_c) for both samples were studied† in pure CO_2 at 288 K, 50–360 bar with 0.25 g dm^{-3} NPs. This was done by visual inspection; the appearance of the cell was noted both when stirred and unstirred in order to confirm dispersion of the sample. The AOT-coated NPs displayed negligible solubility, appearing opaque throughout the pressure range with large aggregates clearly visible. Conversely, the TC14-coated sample was better dispersed, displaying a notably improved clarity above P_c = 80 bar.[17] Solvent quality was then improved by addition of *n*-heptane co-solvent[18] (10% vol)[19] and the samples were assessed as before.† Even in this mixed solvent and with vigorous stirring, the AOT-coated NP sample displayed little solubility: cell contents appeared opaque throughout the range studied. However, the solution of TC14-coated CeO_2 NPs in the mixed solvent exhibited transparency, with P_c = 120 bar.[17]

UV-Vis spectroscopy was used to assess the solubility of the AOT- and TC14-coated NPs in the CO_2 rich solvent. Samples were delivered into the cell *via* a gauze cradle suspended from a piston well above the cell windows.† The samples were subject to the same conditions: vigorous stirring, 303 K, 300 bar (to be above P_c), and absorbance was monitored as a function of time in the range 300–400 nm (Fig. 3). For the AOT sample in the CO_2–heptane mixture initial absorbance was low and did not change up to 3 h, indicating minimal incorporation of AOT-CeO_2 NPs. Next, TC14-CeO_2 NPs were tested both in pure CO_2 and in the mixed solvent. In pure CO_2, little absorbance was detected up to 12 h† but interestingly with the CO_2–heptane mixture strong absorbance was initially seen, consistent with well-dispersed CeO_2 NPs. For this latter system the intensity increased with time; after 12 h the dispersed concentration was consistent with an uptake of approximately 10% of the original NPs in the gauze.[19]

These results show successful stabilization of CeO_2 NPs in a CO_2-rich solvent. The stabilizing organic layer is the only major difference between the two studied systems, permitting isolation of surfactant structural effects. The tri-chain surfactant TC14 is clearly an excellent model on which to base hydrocarbon surfactant design for dispersion of NPs in CO_2-containing solvents. The combination of three ^{t}Bu tips maximises the methyl chain tip density, known to be a key factor in lowering the solute/solvent surface energy.[11]

This work is financially supported by the EPSRC, the University of Bristol DTA and by Kodak.

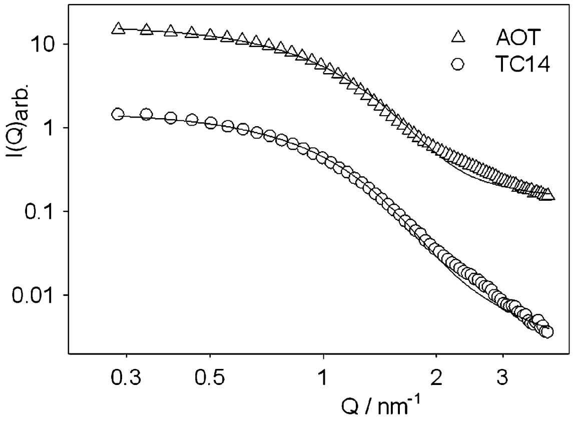

Fig. 2 SAXS data (symbols) and form factor fits (lines) for as-prepared surfactant-coated CeO_2 NPs in heptane. Note *I*(*Q*) is plotted on an arbitrary scale and the AOT data have been shifted by a factor of 10 for clarity.

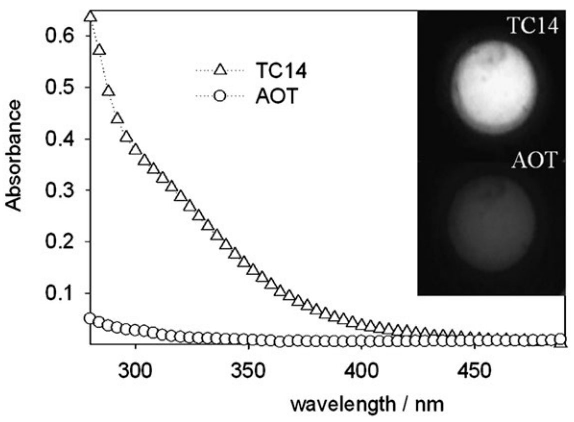

Fig. 3 UV-Vis spectra of AOT- and TC14-coated CeO_2 NP samples in 9 : 1 CO_2 : heptane by volume at 303 K, 300 bar (samples introduced *via* a gauze cradle). Photographs show sample appearance at 288 K, 300 bar (samples placed directly into cell).

Notes and references

1 *Catalysis by Ceria and Related Materials*, ed. A. Trovarelli, Imperial College Press, London, 2002.

2 T. X. T. Sayle, S. C. Parker and D. C. Sayle, *Phys. Chem. Chem. Phys.*, 2005, **7**, 2936.

3 S.-Y. Lai, Y. Qiu and S. Wang, *J. Catal.*, 2006, **237**, 303; S. Imamura, H. Yamada and K. Utani, *Appl. Catal., A*, 2000, **192**, 221.

4 T. Masui, K. Fujiwara, Y. Peng, T. Sakata, K. Machida, H. Mori and G. Adachi, *J. Alloys Compd.*, 1998, **269**, 116.

5 M.-P. Pileni, *Nat. Mater.*, 2003, **2**, 145; J. Eastoe, M. J. Hollamby and L. Hudson, *Adv. Colloid Interface Sci.*, 2006, **5**, 128.

6 A. Bumajdad, M. I. Zaki, J. Eastoe and L. Pasupulety, *Langmuir*, 2004, **20**, 11223.

7 Z. Wu, R. E. Benfield, L. Guo, H. Li, Q. Yang, D. Grandjean, Q. Li and H. Zhu, *J. Phys.: Condens. Matter*, 2001, **13**, 5269.

8 S. Sathyamurthy, K. J. Leonard, R. T. Dabestani and M. P. Paranthaman, *Nanotechnology*, 2005, **16**, 1960.

9 S. Nave, J. Eastoe, R. K. Heenan, D. C. Steylter and I. Grillo, *Langmuir*, 2000, **16**, 8741.

10 S. K. Ritter, *Chem. Eng. News*, 2007, **85**(18), 11; A. Baiker, *Chem. Rev.*, 1999, **99**, 453.

11 J. Eastoe and S. Gold, *Phys. Chem. Chem. Phys.*, 2005, **7**, 1352; J. Eastoe, S. Gold and D. C. Steytler, *Aust. J. Chem.*, 2007, **60**, 630; J. Eastoe, S. Gold and D. C. Steytler, *Langmuir*, 2006, **22**(24), 9832.

12 M. Ohde, H. Ohde and C. M. Wai, *Chem. Commun.*, 2002, 2388; H. Ohde, C. M. Wai, H. Kim, J. Kim and M. Ohde, *J. Am. Chem. Soc.*, 2002, **124**, 4540.

13 P. W. Bell, M. Anand, X. Fan, R. M. Enick and C. B. Roberts, *Langmuir*, 2005, **21**, 11608; M. Anand, P. W. Bell, X. Fan, R. M. Enick and C. B. Roberts, *J. Phys. Chem. B*, 2006, **110**, 14693.

14 S. Gold, J. Eastoe, R. Grilli and D. C. Steytler, *Colloid Polym. Sci.*, 2006, **284**, 1333.

15 R. Aveyard, B. P. Binks, S. Clark, P. D. I. Fletcher, H. Giddings, P. A. Kingston and A. R. Pitt, *Colloids Surf.*, 1991, **59**, 97.

16 S. Gold, PhD Thesis, University of Bristol, Bristol, UK, 2007.

17 The P_c values are slightly lower than previously reported for pure TC14 (ref. 14). Addition of salt to microemulsions is known to affect phase boundaries in heptane (*e.g.* M. Kahlweit, R. Strey, R. Schomacker and D. Haase, *Langmuir*, 1989, **5**, 305), and to lower P_c in pure CO_2 (A. Paul, PhD thesis, University of Bristol, UK, 2001). Therefore in CO_2–heptane mixtures a combination of these effects may result in small P_c shifts.

18 Under these conditions, CO_2 and heptane are fully miscible, *e.g.* J. M. Dobbs, J. M. Wong and K. P. Johnston, *J. Chem. Eng.Data*, 1986, **31**, 303–308.

19 It is important to note that due to the experimental set-up, an increase in pressure goes hand-in-hand with a decrease in cell volume, and therefore a change in the sample concentrations. For example, an increase from 60 bar (just inside the liquid phase of CO_2) to 300 bar feeds through to a volume decrease of ~20%. Therefore, in this work reported concentrations and solvent compositions must be taken as approximate, although they do not alter by more than 25%.