Ostwald-Ripening of Cobalt Precipitates in Silica Aerogels ? - An Ultra-Small Angle X-Ray Scattering Study

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Monolithic silica aerogels with radial symmetry were synthesized by supercritical drying, doped to 2\% and 10\% with cobalt and reduced with hydrogen. All samples were investigated with ultra small angle X-ray scattering. The non-doped aerogels have three populations of scatterers with radii of gyration of about 1, 4, and 6 - 7 nm. The doped aerogels show an additional structure with a radius of gyration ranging from 105~nm to 300~nm. This structure causes intensity oscillations, thus revealing a relatively narrow size distribution. Scattering curves of the 10\% doped aerogels fitted well to a Lifshitz-Slyozov-Wagner particle size distribution, thus revealing that Ostwald ripening might have occurred during aerogel preparation. The same range shows also differences depending on whether the samples were reduced, or in their as-prepared condition. Scattering curves obtained from the cylinder axis region were different from the scattering curves obtained from the sample boundary, indicating a process-dependent skin effect.

Motivation

- Highly disperse metal nano-particles for catalysis applications such as Fischer-Tropsch synthesis, embedded in high-surface area aerogels.

Sample preparation

Undoped and Co doped silica aerogels were prepared by modifications of published procedures [Russo,Casula]. Briefly, a sol of tetramethoxysilane (TMOS, Aldrich, 98%) in methanol was prepared by combining 15 mL each of TMOS and methanol. A solution of water, methanol, and NH4OH was prepared from 7.5 mL of methanol, 6 mL of water, and 0.750 mL of 2.8 % NH4OH. The solutions were combined with vigorous stirring, transferred into cylindrical polyethylene forms, and allowed to gel. The gels were aged in their sealed forms for three days. For undoped gels, the gels were removed from their forms and solvent exchanged with absolute ethanol. The ethanol was exchanged for acetone. The acetone-filled gel was placed in an acetone-filled 500 mL autoclave and the acetone was replaced with liquid CO2. The autoclave was heated to 60 C to transform the CO2 into a supercritical fluid. The autoclave was cooled to room temperature and the aerogel removed. The volume of the aerogel was approximately 90 % of the original gel and remained monolithic through the entire process. For Co doped aerogels, the wet gels were solvent exchanged with absolute ethanol three times for at least three hours each time. The gels were then loaded with Co(NO3)2 by exchanging the absolute ethanol with a solution of Co(NO3)2 dissolved in ethanol. Concentration and volume of the cobalt containing ethanol solution was chosen such that the cobalt concentration in the final aerogel would be 2% or 10%, respectively. The aerogels produced showed the same reduction in volume as the CO2 dried gels, were monolithic, and showed an unusual radial color variation. The color is caused by oxides of cobalt that result when Co(N03)2 is heated above its decomposition temperature. Both the undoped and Co-doped aerogels were calcinated in static air at 737 K for 12 hours and the Co-doped aerogels were reduced in a flowing stream of hydrogen at 737 K for 4 hours.

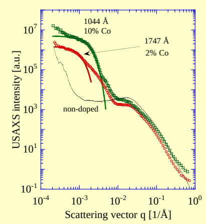
USAXS

Ultra-small angle X-ray scattering (USAXS) was carried out at synchrotron radiation beamline 33-ID at UNICAT, Advanced Photon Source, Argonne National Laboratory. At this beamline, a Bonse-Hartset-up allows one to record USAXS scattering curves (SC) using a photo diode detector with an angular resolution of 0.0001 1/Å at a q-range from 0.0002 1/Å to 1.0 1/Å. The upper resolution range is 5,000 Å. The scattering vector q is a typically used quantity in small angle scattering and relates to the diffraction angle 2θ, as known from X-ray diffraction, via the relation q = 4 π λ / sin θ with X-ray wavelength λ. The data acquisition time for a SC with 150 data points was typically 15 minutes per sample. SC were recorded at X-ray energies of 7695 eV and 7710 eV, with the ultimate aim to make anomalous scattering. All USAXS data were fully corrected for all instrumental effects, including background subtraction and desmearing. The samples came in cylinder-like shape and were cut in cylinder fragments with a thickness of approximately 1~cm. Accurate sample thickness data are not known, and scattered intensities are thus given in arbitrary units. For skin studies, either the cylinder center (= no skin) or the cylinder boundary (= skin) was positioned in the X-ray beam, with the cylinder axis parallel to the X-ray beam. For all other cases, the cylinder axis of the sample was perpendicular to the beam, and the sample thickness at this position was at maximum.

Sample matrix

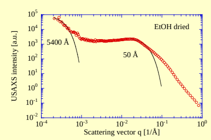
Not-Reduced	Reduced
0% Co 7695 eV / 7710 eV	0%Co 7695 eV / 7710 eV
2% Co 7695 eV / 7710 eV	2% Co 7695 eV / 7710 eV
10% Co 7695 eV / 7710 eV	10% Co 7695 eV / 7710 eV

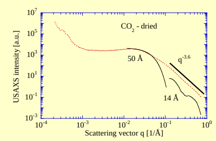
Doped vs. Non-doped aerogel



Scattering curves of aerogels exhibit plateau around q=3*10^{-3} 1\Å, which is pronounced for the undoped aerogel. Doped aerogels have a shorter such plateau and a pronounced structure from objects of 1000 and 2000 Å size, depending on doping level. This structure is probably present in the non-doped samples, but with a larger size, as indicated by the steep increase of USAXS intensity for very small q-vectors. Interestingly, lower dopant level produces larger structures, which suggest a gradual filling of pores with cobalt

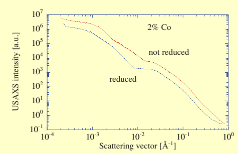
CO2-dried vs. EtOH dried aerogel





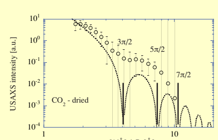
No significant changes in the scattering curves were found depending on whether they were dried with CO2 or with EtOH.

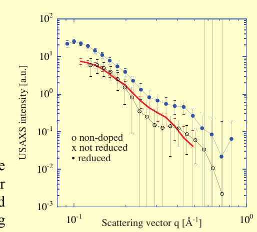
Co-aerogel vs. reduced Co-aerogel



Reduction of the aerogels caused a remarkable change in the scattering curves. Reduction typically causes shrinking of the metals due to change from oxidic phase to metal phase, as observed here at q=5*10-3 1\Å

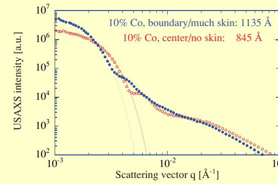
Fitting with sphere structure factor

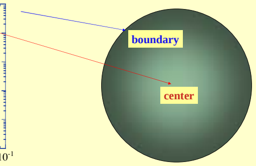




Scattering curves of aerogels could be fitted with Rayleigh structure factor for spheres at low q-vectors, indicated by dips in the original scattering curves at half integer multiples of π.

Center vs. Skin in aerogel





Aerogels were homogeneous in azimuthal, but not in radial direction. Gradient in microstructure was found by directing beam to the sample center (no skin), and to the sample boundary (skin). For the low q-values, the center had smaller particles than the boundary.

LSW distribution

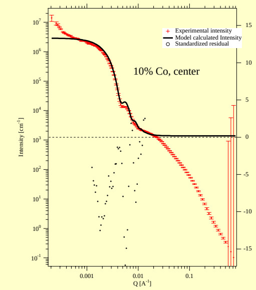
Sample	Finest level	Level 2	Level 3	Largest level
Parameters	R_g [Å]	R_g [Å]	R_g [Å]	Mean diameter; FWHM [Å]
CO_2 dried, non-doped	4.7±3.5	34.5±1.6	71.5±2.5	N.A.
EtOH dried, non-doped	11.0±2.8	46.6± -	55.0±5	N.A.
10% Co, no skin	10.6±1.0	46.7±0.3	64.5±3.5	1880; 611
10% Co, skin	7.5±30.3	21.9±1.7	80.6±1.4	2248; 1189
10% Co, not reduced	6.1±1.1	17.1±0.5	72.4±1.0	1501; 1627
10% Co, reduced	6.4±0.7	17.7±0.5	68.1±0.7	~ 2100
10% Co, not reduced	7.2±0.8	20.0±1.6	68.1±1.3	~ 2127
2% Co, reduced	7.3±1.3	18.0±0.6	62.8±0.7	~ 3000
2% Co, not reduced	6.4±0.6	17.6±0.4	63.0±1.2	~ 2400
2% Co, 7695 eV, red.	8.9± -	25.3± -	61.1± -	~ 1000, 2000, 4400
2% Co, 7695 eV, not red.	8.2±0.8	18.1±0.61	68.2±1.1	~ 2400
10% Co, 7710 eV, red.	7.4±0.6	29.1±4.5	67.0±3.9	~ 2200
10% Co, 7710 eV, not red.	8.3±1.5	20.6±2.0	68.2±1.4	~ 2210
2% Co, 7710 eV, red.	4.5±0.9	36.1±1.7	66.4±3.7	more populations
2% Co, 7710 eV, not red.	4.8±0.7	36.6±1.7	73.6±2.3	~ 2253

0.1 Quantitative analysis with unified fit and LSW size distribution

$$I(q) = G \exp\left(\frac{-q^2 R_g^2}{3}\right) + B\left(\left(erf\left(\frac{qR_g}{\sqrt{6}}\right)\right)^3 / q\right)^P \quad (1)$$

The LSW distribution reads as follows:

$$P(R) = \frac{3^4 R^2 \exp\left(-\frac{1}{1-\frac{2R}{3}}\right)}{2^{\frac{5}{3}} (R-3)^{\frac{7}{3}} \left(\frac{3}{2} - R\right)^{\frac{11}{3}}} \quad (2)$$



Scattering curves could be fitted best at low q-vectors with a LSW-particle size distribution, suggesting that Ostwald ripening was taking place in the aerogels.

Anomalous USAXS

We have attempted anomalous USAX on these samples in order to separate the scattering of the cobalt from the scattering of the aerogel matrix. Results were not unambiguously; more beamtime would have been necessary to address this issue.

References

[1] Artur Braun, Jan Ilavsky, Brian C. Dunn, Peter E. Jemian, Frank E. Huggins, Edward M. Eyring, Gerald P. Huffman. *Oswald-Ripening of Cobalt Precipitates in Silica Aerogels? - An Ultra-Small Angle X-Ray Scattering Study.* J. Appl. Cryst. **38**: 132-138 Part 1 FEB 2005.

[2] Brian C. Dunn, Paul Cole, Daniel Covington, Matthew C. Webster, Ronald J. Pugmire, Richard D. Ernst, Edward M. Eyring, Naresh Shah, Gerald P. Huffman, Silica aerogel supported catalysts for Fischer–Tropsch synthesis, *Appl. Catal. A*, 278(2) (2005) 233-238.

[3] Nimir O. Elbashir, Prasanta Dutta, A. Manivannan, Mohindar S. Seehra, Christopher B. Roberts, Impact of cobalt-based catalyst characteristics on the performance of conventional gas-phase and supercritical-phase Fischer–Tropsch synthesis, *Appl. Catal. A*, 285(1-2) (2005) 169-180.

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