

# USAXS Studies on Cobalt-doped Aerogel Catalysts

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## Introduction

Cobalt-doped silica aerogels with 2% and 10% doping levels were investigated with ultrasmall-angle x-ray scattering (USAXS). Aerogels are high-surface-area materials that can basically serve as hosts for highly disperse metal particles and thus be employed as catalysts. Nondoped aerogels showed a relatively rich structure, having three different size levels, ranging from about 0.5 to 1, 2 to 5, and 6 to 8 nm. In addition, the doped aerogels show a pronounced structure, with sizes ranging from 100 to 400 nm, depending on the sample chosen. The size distribution was relatively sharp. It was possible to acquire scattering curves (SCs) from both the center and boundary of the cylindrical, monolithic aerogel samples and thus find a skin effect.

## Methods and Materials

Undoped and Co-doped silica aerogels were prepared by using modified established and published procedures. Briefly, a solution of tetramethoxysilane (TMOS) in methanol was prepared by mixing TMOS and methanol. A solution of water, methanol, and  $\text{NH}_4\text{OH}$  was prepared. Both solutions were combined via vigorous stirring, transferred into cylindrical polyethylene forms, and allowed to gel. For undoped gels, the gels were removed from their forms and solvent-exchanged with absolute ethanol, and the ethanol was exchanged for acetone. The acetone-filled gel was placed in an acetone-filled autoclave, then the acetone was replaced with liquid  $\text{CO}_2$ . The autoclave was heated to  $60^\circ\text{C}$  to transform the  $\text{CO}_2$  into a supercritical fluid. While the temperature was maintained above the critical temperature, pressure inside the autoclave was released over a period of 4 hours. The autoclave was cooled to room temperature, and the monolithic aerogel was removed.

For Co-doped aerogels, the wet gels were solvent-exchanged with absolute ethanol. The gels were then loaded with  $\text{Co}(\text{NO}_3)_2$  by exchanging the absolute ethanol with a solution of  $\text{Co}(\text{NO}_3)_2$ , with concentrations targeted at 2% and 10%. After a single solvent exchange, the gels were loaded into an autoclave filled with ethanol and purged with  $\text{N}_2$ . The autoclave was heated in a fluidized sand bath at pressures that allow the methanol to be a

supercritical fluid. While the autoclave was kept at  $300^\circ\text{C}$ , the pressure was slowly released over a period of 2 hours, then the autoclave was removed from the sand bath and allowed to cool in static air until room temperature was achieved. The aerogels produced in this manner showed the same reduction in volume as the  $\text{CO}_2$  dried gels, were monolithic, and showed an unusual radial color variation. The color was caused by oxides of cobalt that result when  $\text{Co}(\text{NO}_3)_2$  is heated above its decomposition temperature. Undoped and Co-doped aerogels were calcined at  $500^\circ\text{C}$ , and the Co-doped aerogels were reduced in hydrogen at  $500^\circ\text{C}$ .

USAXS was carried out at UNI-CAT beamline 33-ID at the APS at x-ray energies of 7710 and 7695 eV. These energies are before and above the cobalt K-edge x-ray absorption edge. At this beamline, a Bonse-Hart setup allows one to record USAXS SCs by using a photodiode detector with an angular resolution of  $0.0001 \text{ \AA}^{-1}$  at a q-range of 0.0001 to  $1.0 \text{ \AA}^{-1}$  [1]. The SCs were desmeared and background-corrected with the beamline-specific software.

## Results

Figure 1 shows SCs of undoped (left) and 10% Co-doped (right) aerogel samples. The SC of the undoped sample reveals three size ranges and is fitted with a unified fit approach [2]. The radii of gyration are  $4.7 \pm 3.5 \text{ \AA}$  and  $34.5 \pm 1.6 \text{ \AA}$  for the two smallest populations of voids or pores. These have exponents of decay close to 4 and thus represent voids with smooth surfaces. The next larger population is  $71.5 \pm 2.5 \text{ \AA}$  with an exponent of decay of 3. The doped samples show these size ranges as well, but most significant is the fact that the doped aerogel has an additional hump at low scattering vectors Q between 0.001 and  $0.01 \text{ \AA}^{-1}$ . This is observed for all doped samples. The smaller hump at  $0.006 \text{ \AA}^{-1}$  is not an additional structure but is the second-order peak of the first structure and thus indicates a relatively narrow size distribution for this population.

The pronounced hump at very low Q is bent down for the reduced samples, with an exponent of decay close to 3. This is apparent from Fig. 2 (left). However, the following part of the SC from  $0.003$  to  $0.007 \text{ \AA}^{-1}$  is

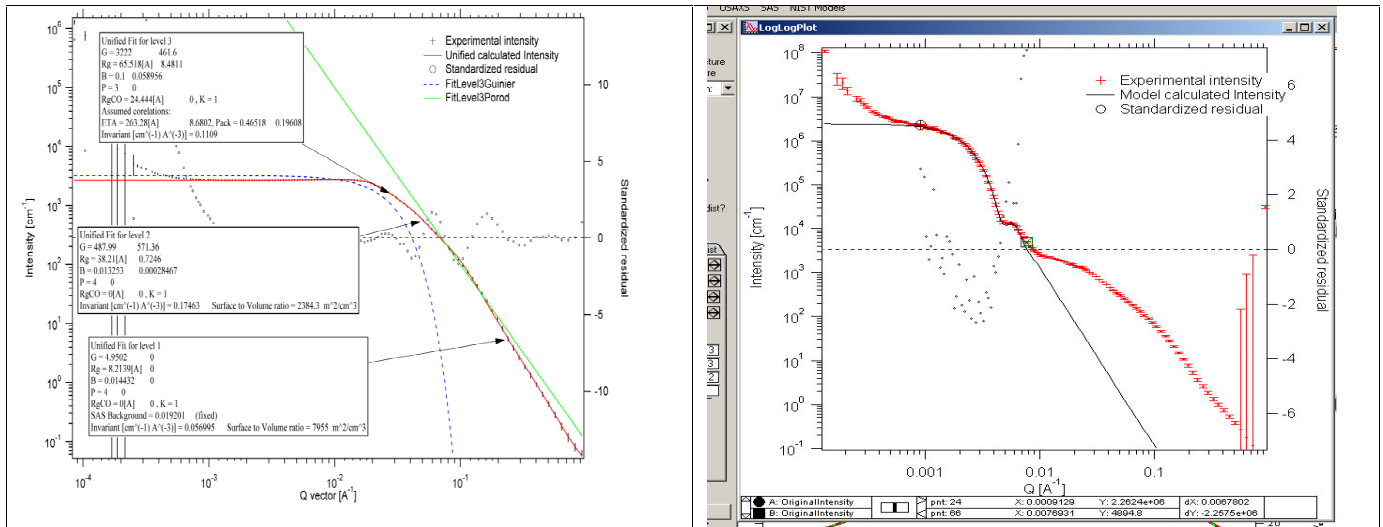


FIG. 1. SCs of undoped aerogel (left) and 10% cobalt-doped aerogel (right). Drawn solid lines are unified fit or structure factor of spherical particles with Gaussian size distribution, respectively.

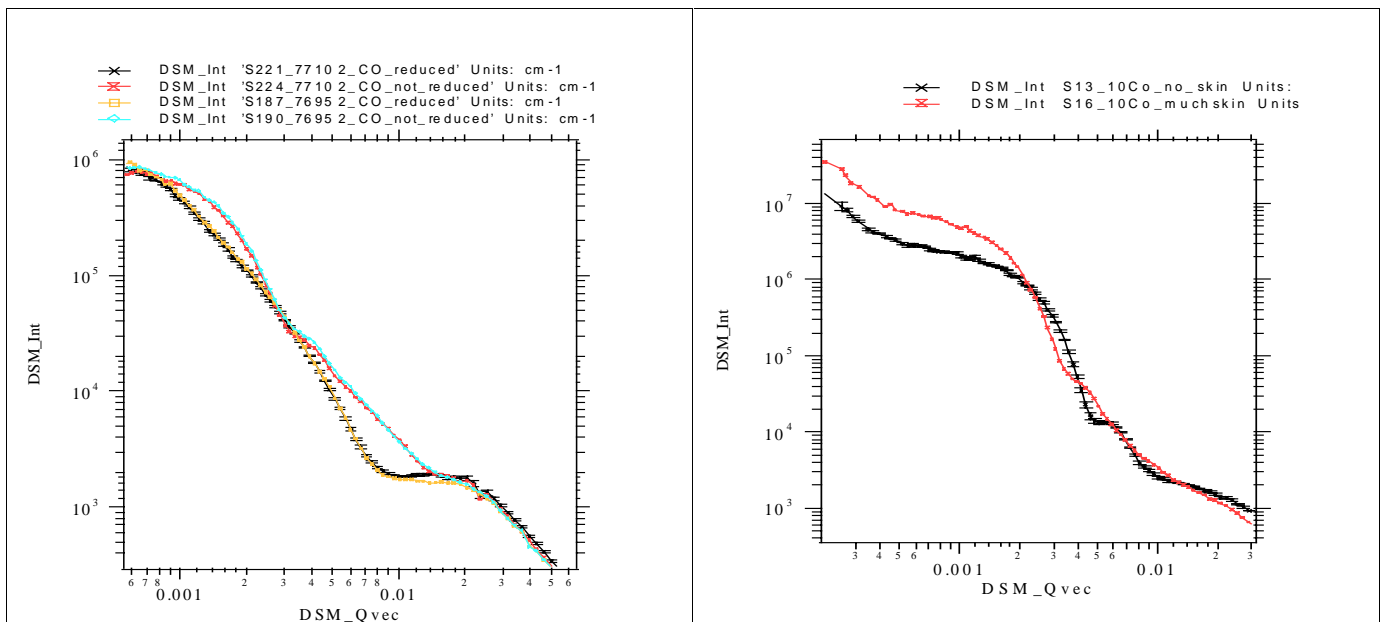


FIG. 2. Graph on left shows SCs of 2% Co-doped oxidized aerogel (closed square = 7710 eV, diamond = 7695 eV; the two “upper curves”) and reduced aerogel (x = 7710 eV, open square = 7695 eV; the two “lower curves”). Graph on right shows SCs of 10% Co-doped aerogel from sample radial center (x) and from boundary/skin (closed square).

steeper for the reduced samples and close to an exponent of decay of 4. Reduction thus causes structural transformations in the cobalt, as is typically observed and expected. It is remarkable, however, that characteristic bending points in the SC, such as at 0.0008, 0.003, 0.005, and 0.03 retain their position during reduction. It is therefore possible that upon reduction, the center of mass

of the particles does not change, but their geometry does. A typical observation is that oxidized nanoparticles shrink during reduction.

We attempted to make a quantitative anomalous small-angle x-ray scattering (ASAXS) analysis, but because of time restrictions, SC could be obtained at only two x-ray energies, which was not sufficient for a meaningful

analysis. ASAXS is generally useful for the study of this kind of material because it permits one to distinguish between voids or pores and cobalt precipitations — a discrimination that cannot be directly and unambiguously made without ASAXS.

The doped aerogels showed a radial color variation. We thus took SC from the center and from the boundary of one sample. Both SCs are shown in the image on the right in Fig. 2. The SC from the sample’s center (x symbols) is shifted toward larger Q values than the SC taken from the boundary. Thus, the center (no skin) contains smaller Co precipitates than the sample boundary (much skin). Quantitative data are provided in Table 1, which shows the radii of gyration for the first three populations of scatterers as well as the large size population with intensity minima and sharp size distribution.

## Discussion

USAXS is a useful technique for studying aerogels doped with metals for use as catalysts. The SCs of aerogels are rich in structure. Four different size populations were found, and the effect of doping and reduction — necessary steps for catalyst preparation — can be monitored with quantitative significance. Radial inhomogeneity of the sample can be studied by recording SCs from the center and boundary of the sample. This permits investigations of whether this catalyst system is prone to Liesegang pattern formation, for instance. With little more experimental effort, ASAXS is also possible, and it will allow investigation of multicomponent

catalysts, such as alloys. In addition, supporting experiments such as transmission electron microscopy x-ray absorption spectroscopy, and x-ray diffraction are in progress.

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## References

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TABLE 1. Quantitative data.

Sample	$R_g$ (Å)	$R_g$ (Å)	$R_g$ (Å)	$R_o$ (Å)	Width (Å)
10% Co, no skin	$10.6 \pm 1.0$	$46.7 \pm 0.3$	$64.5 \pm 3.5$	1880	611
10% Co, much skin	$7.5 \pm 0.3$	$21.9 \pm 1.7$	$80.6 \pm 1.4$	2248	1189