Characterization of Dry-Air Aged Granules of Silver-Functionalized Silica Aerogel

Fuel Cycle Research & Development

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SUMMARY

Recently, samples of Ag^0-functionalized silica aerogel were "aged" in flowing dry air for up to 6 months and then loaded with iodine. This dry-air aging simulated the impact of long-term exposure to process gases during process idling. The 6-month aged sample exhibited an iodine sorption capacity of 32 mass%, which was 22 relative percent lower than that for an un-aged Ag^0-functionalized silica aerogel. The exactly same test with a 6-month aged silver mordenite, a current baseline technology for capturing iodine, resulted in the loss of 40 relative percent of sorption capacity. In an attempt to understand this decrease in sorption capacity, we characterized physical properties of the aged aerogel samples with Brunauer-Emmett-Teller (BET) nitrogen adsorption, X-ray diffraction (XRD), and high resolution scanning electron microscopy (SEM). The results showed no detectable impact of aging on the aerogel microstructure or the silver nanoparticles in the aerogel, including their spatial distribution and morphology.

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ABBREVIATIONS

BET	Brunauer-Emmett-Teller
FTIR	Fourier transform infrared
ICCD	International Center of Crystallographic Data
ICP-MS	inductively coupled plasma mass spectrometer
ICSD	International Center of Structure Data
ORNL	Oak Ridge National Laboratory
PDF2	powder diffraction file 2
PNNL	Pacific Northwest National Laboratory
SEM/EDS	scanning electron microscopy-energy dispersive spectroscopy
TEM	transmission electron microscopy
XRD	X-ray diffraction

1 INTRODUCTION

The solid sorbents for capturing radioiodine from reprocessing off-gas streams are required to have a high sorption capacity and selectivity for iodine. These properties should be predictable with time when the plant is idling and sorbent is exposed to heated air containing water vapor and possibly NO and NO_2 gases. Ideally, these properties will not decrease significantly as that would create a need for more material and either larger filters or more frequent change-outs.

An advanced sorbent, a silver-functionalized silica aerogel, is being developed at Pacific Northwest National Laboratory (PNNL) for capturing and immobilization of iodine from gaseous products of nuclear fuel reprocessing (Matyáš et al. 2011 and 2012). The lab-scale testing of this sorbent under prototypic off-gas conditions demonstrated decontamination factors in excess of 10 000 (Soelberg et al. 2012) and sorption capacity of 48 mass% (Strachan et al. 2011). Recently, samples of Ag^0-functionalized silica aerogel were "aged" in flowing dry air for up to 6 months and then loaded with iodine. Dry-air aging simulated the impact of long-term exposure to process gases during process idling. The 6-month aging resulted in an iodine sorption capacity 32 mass%, which was 22 relative percent lower than that for an un-aged Ag^0-functionalized silica aerogel (41 mass%) (Bruffey et al. 2012). The exactly same test with a 6-month aged silver mordenite, a current baseline technology for capturing iodine, resulted in the loss of 40 relative percent of sorption capacity (Jubin et al. 2010).

In this study, an effort was made to assess the impact of aging on the physical properties of silica aerogel backbone and Ag^0 nanoparticles. The specific surface area, total pore volume and average pore size of aged Ag^0-functionalized silica aerogel were measured with BET nitrogen adsorption. Phase analyses were performed with XRD and high resolution SEM was used to investigate spatial distribution and morphologies of Ag^0 nanoparticles.

2 METHODS AND RESULTS

2.1 Surface Area and Pore Size Measurements

The analyses were performed on samples degassed at 25 °C under vacuum. The data from nitrogen adsorption/desorption at 77 K were collected with a Quantachrome Autosorb 6-B gas sorption system (Quantachrome Instruments, Boynton Beach, FL). The surface area was determined from the isotherm with the five-point BET method (Lowell and Shields 1991). The Barrett–Joyner–Halenda (BJH) method (Barrett et al. 1951) was used to calculate the total pore volume and pore size distribution including average pore diameter.

Figure 1 shows Type IV isotherms for Ag^0-functionalized aerogel granules that were aged in dry air for 0 and 6 months. The isotherms that are typical for mesoporous materials (pore sizes from 2 to 50 nm) exhibit essentially the same shape, including a small adsorption/desorption hysteresis. The relatively small degree of hysteresis indicates that the energetics of the pore-filling and -emptying processes are similar in nature. Table 1 shows the surface area, total pore volume, range of pore sizes, and average pore size for adsorption and desorption for granules of Ag^0-functionalized aerogel that were aged in dry air for 0, 1, 2, 4, and 6 months. The surface area, pore volume, range of pore sizes, and average pore size for adsorption and desorption were unchanged with aging time, indicating a good long-term microstructure stability of the aerogel.

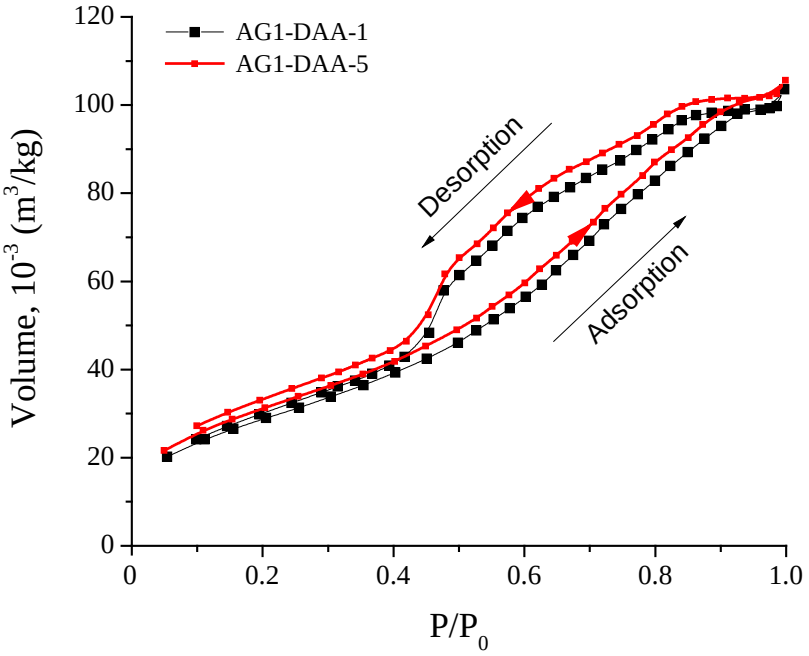

Figure 1. Adsorption/Desorption Isotherms for un-aged (AG1-DAA-1) and 6-month aged (AG1-DAA-5) samples of Ag^0-functionalized aerogel

Table 1. Surface area, total pore volume, range of pore sizes, and average pore size for adsorption and desorption for Ag^0-functionalized aerogel aged in a dry air stream for 0 (AG1-DAA-1), 1 (AG1-DAA-2), 2 (AG1-DAA-3), 4 (AG1-DAA-4), and 6 (AG1-DAA-5) months.

Sample ID	Surface area, m^2/g	Total pore volume, 10^{-3} m^3/kg	Range of pore sizes, nm	Average pore size, (Ads/Des), nm
AG1-DAA-1	106.4	0.17	2-20	6/5
AG1-DAA-2	116.8	0.16	2-20	6/5
AG1-DAA-3	115.1	0.16	2-20	6/5
AG1-DAA-4	117.7	0.16	2-20	6/5
AG1-DAA-5	114.2	0.17	2-20	6/5

2.2 Phase Identification

The XRD analyses were performed on powdered samples on a zero-background silicon holder. Diffraction patterns were obtained with a Bruker D8 Advanced diffractometer (Bruker AXS, Madison, WI) equipped with a Cu K_α X-ray target ($\lambda = 0.15406$ nm), goniometer radius of 250 mm, 0.3° fixed divergence slit, and LynxEye™ position sensitive detector with an angular range of 3° 2-theta. The scan parameters were 0.03° 2-theta step size, 4 s dwell time, and 30 to 60° 2-theta range. Jade 6.0 software (Materials Data Inc, Livermore, CA, USA) and both the International Center of Crystallographic Data (ICCD) powder diffraction file 2 (PDF2) released in 1999 and the International Center of Structure Data (ICSD) released in 2004 were used to identify crystalline phases.

Figure 2 shows an X-ray diffraction pattern of aged aerogel samples with Ag^0 as the only identified phase. This suggests a good long-term stability of Ag^0 nanoparticles in dry air stream. However, we cannot rule out the conversion of some of the Ag to Ag_2O, since the amount of Ag_2O might be near the detection limit of our XRD (~ 0.1 wt%). In addition, Ag_2O might be present in the form of sub-nano sized areas hardly detectable by XRD.

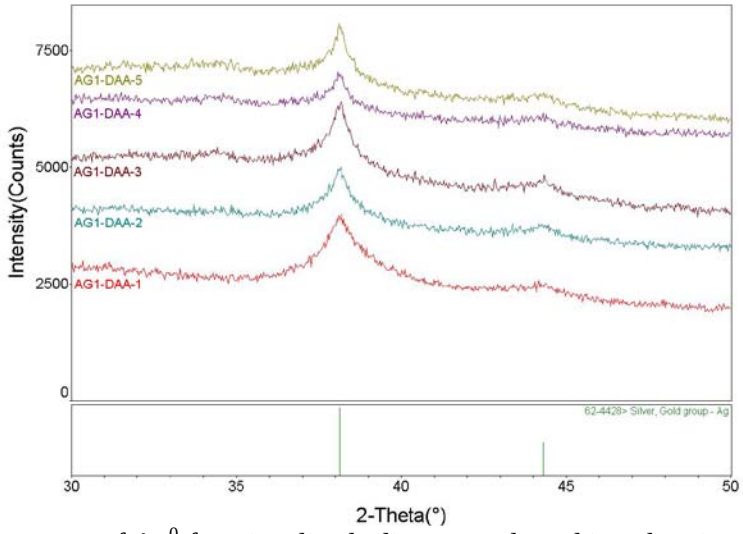

Figure 2. The XRD patterns of Ag^0-functionalized silica aerogel aged in a dry air stream for 0, 1, 2, 4, and 6 months, AG1-DAA-1 to AG1-DAA-5, respectively.

2.3 Microstructure Analysis

Selected granules of aged aerogels were embedded in epoxy and cured at 60 °C for 24 h. The small sections were cleaved with a microtome knife and then deposited on copper grids and carbon coated. The samples were characterized with a SEM JSM-7001F/TTLS (JEOL Ltd., Tokyo, Japan) equipped with a field emission gun and capable of examining specimens under variable pressure conditions, allowing them to be evaluated without a conductive coating.

Figure 3 shows Ag^0-functionalized silica aerogel before and after aging for 6 months in dry air. The spatial distribution and morphology of silver nanoparticles was unchanged.

A B

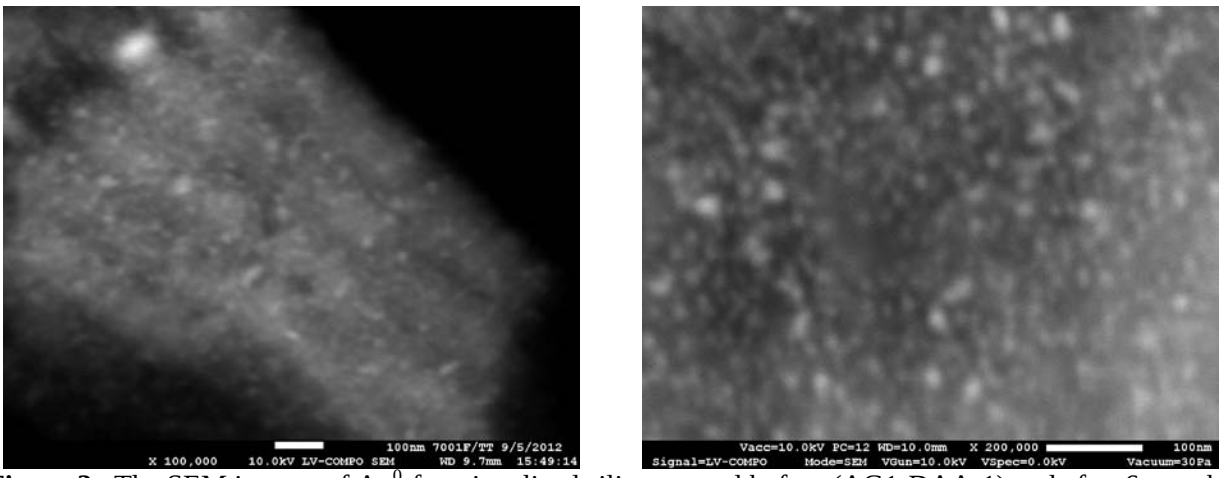

Figure 3. The SEM images of Ag^0-functionalized silica aerogel before (AG1-DAA-1) and after 6 months aging in dry air stream (AG1-DAA-5), A and B, respectively; white features are Ag^0 nanoparticles, gray area is silica aerogel backbone.

3 CONCLUSIONS

We characterized samples of Ag-functionalized silica aerogel after aging in dry air for up to 6 months. The aging and iodine loading of these materials was carried out at Oak Ridge National Laboratory (ORNL) (Bruffey et al. 2012). The observed 9 mass % decrease in sorption capacity for a 6-month aged Ag^0-functionalized silica aerogel cannot be explained from the data reported here. The experimental investigations showed no impact of aging on the aerogel microstructure or the silver nanoparticles in the aerogel, including their spatial distribution and morphology. However, we cannot rule out the conversion of some of the Ag to Ag_2O, since the amount of Ag_2O might be near the detection limit of our XRD under the conditions the patterns were obtained. In addition, Ag_2O might be present in the form of sub-nano sized areas hardly detectable by XRD. Examination in a transmission electron microscope (TEM) with selected area diffraction, might resolve this uncertainty.

In the next phase of the project, samples of Ag^0-functionalized silica aerogel will be exposed to flowing moist air for up to 6 months and characterized before and after iodine loading for physical characteristics, crystalline phases, and spatial distribution and morphologies with even larger array of experimental techniques, e.g., TEM, Fourier transform infrared microscopy, and inductively coupled plasma mass spectrocopy, to reveal features/factors hindering the sorption performance.

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