# Radioactive Iodine Capture in Silver-Containing Mordenites through Nanoscale Silver Iodide Formation

Karena W. Chapman,*,† Peter J. Chupas,† and Tina M. Nenoff‡

*X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois, 60439 and Sandia National Laboratories, Surface and Interface Sciences, Albuquerque, New Mexico 87185*

Received April 13, 2010; E-mail: chapmank@aps.anl.gov

Safe nuclear energy is inevitably linked to the safe storage of nuclear waste. As such, extreme selectivity and durability are critical to materials used in nuclear separations and long-term waste storage. $^{129}$I is one of the radionucleotides that remains of strong interest and concern. While this radionucleotide is only found in small concentrations in nuclear effluent, the effective capture and storage of iodine is critically important to public safety due to its involvement in human metabolic processes and its long half-life ($\sim 10^7$ years).[1] The leading approach to capture radioactive gaseous byproduct such as iodine during nuclear fuel reprocessing involves sorption onto silver-containing zeolites. Indeed, for many decades the silver-containing zeolite mordenite (MOR, Figure 1) has been a benchmark for radiological iodine capture; however, the molecular basis for its performance remains largely unexplored.[2−4] To rationally optimize the capture process, the subsequent processing for long-term storage and, ultimately, to develop the next generation of iodine capture materials, it is first important to understand the distribution and properties of the iodide formed (silver iodide) and the role of the zeolite support. While the phase behavior of bulk AgI is well established (the ambient two-phase mixture of $\beta$- and $\gamma$-polymorphs transforms to the (super) ion-conducting $\alpha$-phase above 147 °C, Figure 1),[5−8] as often occurs, that behavior can differ for supported and nanoscale material.[9] This includes the proposed existence of an "amorphous-like" interfacial structure and the depression of the $\alpha$-to-$\beta/\gamma$ transition temperature upon cooling.[10−14]
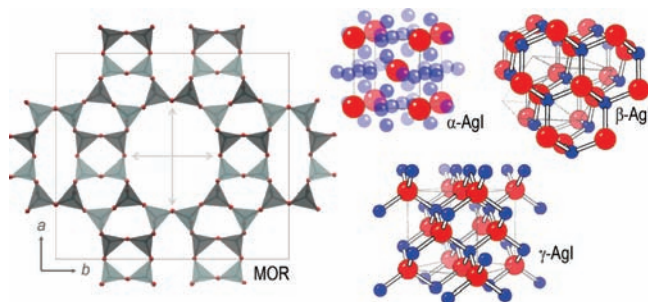


**Figure 1.** MOR structure and $\alpha$-, $\beta$-, and $\gamma$-AgI polymorphs (red, I; blue, Ag). The MOR framework defines one-dimensional channels (12-rings, 6.5 × 7.0 Å$^2$) parallel to the $c$-axis which contain the exchangeable cations and water molecules (omitted for clarity).[15]

Here we present a differential pair distribution function ($d$-PDF) study of I$_2$-treated silver-containing MOR to probe the structure and distribution of the supported AgI—the iodine-capture vehicle. The pair distribution function (PDF) method probes the local structure of nanoscale and amorphous materials, where conventional Bragg crystallographic analysis yields only limited insight. It

provides the distribution of atomic distances within a material, and while not intrinsically chemically specific, by using a differential approach to PDF analysis[16] it is possible to isolate contributions from individual components within a material.[17] This involves subtracting a reference PDF, measured for the host zeolite, from the iodine-loaded system, such that atomic distances from the zeolite can be separated from those in the supported material. It is a standard practice to reduce the Ag$^+$-exchanged MOR prior to use; however, few studies directly compared the reduced and unreduced systems.[18,19] Here, the capture of I$_2$ by both silver-exchanged and reduced silver MOR is investigated.

Silver-exchanged MOR (Ag$^+$-MOR) was derived from a commercial source of sodium MOR (LZM-5Na, UOP Corporation) and reduced under hydrogen (3%, 150 °C, 24 h) to form reduced-silver MOR (Ag$^0$-MOR). Both Ag$^+$-MOR and Ag$^0$-MOR were treated with iodine at an elevated temperature (95 °C, 12 h) to give Ag$^+$-I-MOR and Ag$^0$-I-MOR, respectively. Some of the iodine-free materials were reserved for structural analysis. For comparison, bulk AgI was purchased from Sigma-Aldrich and prepared by iodine treatment of bulk Ag$^0$ metal. Total scattering data suitable for PDF analysis were collected at beamline 11-ID-B at the Advanced Photon Source at Argonne National Laboratory. High-energy X-rays ($\lambda = 0.1370$ Å) were used in combination with a large amorphous-silicon-based area detector to collect data to high values of momentum transfer ($Q_{max} \approx 19$ Å$^{-1}$).[20,21] The PDFs, $G(r)$, were obtained from the total scattering data as described previously (Figure 2).[21] The $d$-PDFs, which isolate the contributions from the supported material, were obtained by direct subtraction of the PDF measured for Ag$^+$-MOR from those for the reduced and I$_2$-treated systems. Fitting of the data and calculation of partial pair contributions were accomplished within PDFfit and PDFgui (Table 1, Figure 2).[22,23]

As anticipated, the data for commercial bulk AgI were consistent with a mixture of $\beta$- and $\gamma$-polymorphs. The PDF data for the I$_2$-treated bulk Ag$^0$ metal indicated incomplete conversion to AgI, with the characteristic features of the face-centered cubic (fcc) metal clearly remaining. While $\beta$-AgI is the thermodynamic product, a $\beta$-AgI/Ag$^0$ model produced a significantly poorer fit than a $\gamma$-AgI/Ag$^0$ model ($R_{fit} \approx 13.5\%$ cf. 7.97%). This suggests that AgI formation through solid−gas reaction favors the $\gamma$-phase.

While the PDFs for the bulk systems contain peaks to large distances, extending beyond 30 Å, the $d$-PDFs for the supported materials are progressively dampened with no discernible features beyond 30 Å (Ag$^0$ and Ag$^0$−I) or 7 Å (Ag$^+$−I). The $d$-PDF for the supported Ag$^0$ was exceptionally well fit by a single phase Ag$^0$ model. The limited $r$-range of the observed peaks (particularly compared to the unconverted Ag$^0$ in the I$_2$-treated bulk metal) suggests that the Ag$^0$ atoms aggregate to form $\sim 3$ nm nanoparticles. As such, the Ag$^0$ atoms are mobile on the MOR surface (at the reduction temperature). This particle size exceeds the dimension

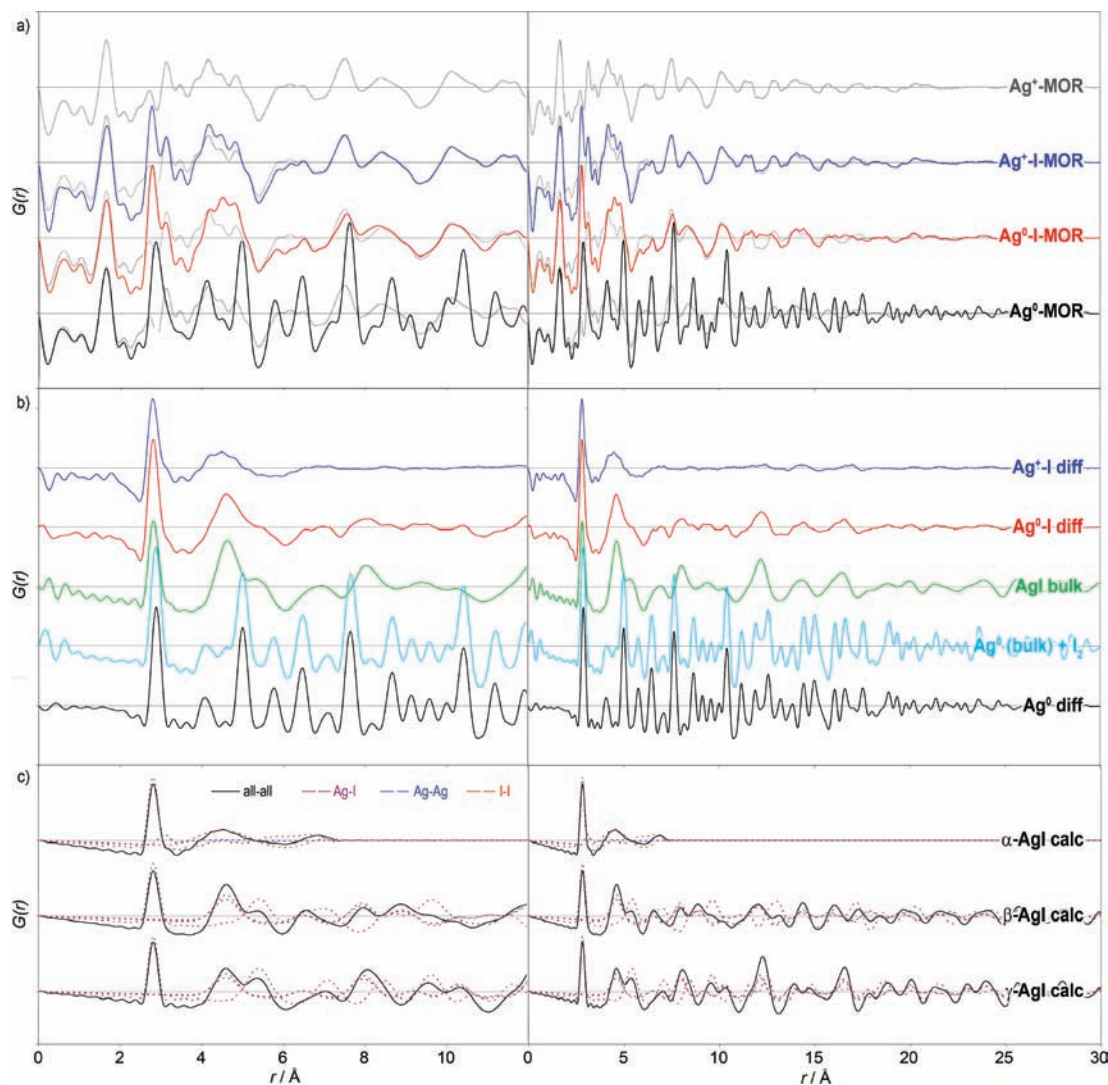**Figure 2.** (a) PDFs for each MOR sample with the reference PDF Ag$^+$-MOR (gray), to be subtracted to recover the $d$-PDFs. (b) $d$-PDFs and PDFs for the bulk AgI samples. (c) Total and partial (Ag−I, Ag−Ag, I−I) PDFs calculated for models of subnanometer α-AgI clusters and β- and γ-AgI.

**Table 1.** Summary of PDF Fitting Results

| | | | | Phase Composition[a] | | | |
|---|---|---|---|---|---|---|---|
| | Form | $r$-range/Å | $R_{fit}$ | Ag$^0$ | α-AgI | β-AgI | γ-AgI |
| Ag$^+$−I | on MOR | 2−10 | 27.5% | − | 1 | − | − |
| Ag$^0$−I | on MOR | 2−30 | 18.0% | − | 0.6 | − | 0.4 |
| AgI (Aldrich) | bulk | 2−30 | 13.6% | − | − | 0.53 | 0.47 |
| AgI (Ag$^0$+I$_2$) | bulk | 2−30 | 7.97% | 0.5 | − | − | 0.5 |
| Ag$^0$ | on MOR | 2−30 | 9.15% | 1 | − | − | − |

[a] Ag$^0$ ($Fm\bar{3}m$, $a = 4.08$ Å); α-AgI ($Im\bar{3}m$, $a = 5.0$ Å, $r < 7$ Å); β-AgI ($P6_3mc$, $a = 4.6$ Å, $c = 7.8$ Å, wurtzite structure); γ-AgI ($F\bar{4}3m$, $a = 6.5$ Å, zinc blende structure).

of the zeolite pores, and the Ag$^0$ particles are presumably localized on the exterior surface of the zeolite. The direct formation of the γ-phase from the reaction of molecular I$_2$ with both nanoscale and bulk Ag$^0$ may be favored because the γ-structure corresponds to the insertion of I$^-$ ions into tetrahedral interstices in the fcc Ag$^0$ lattice. The incomplete conversion of bulk Ag$^0$ suggests that this process may be diffusion limited.

Both Ag$^+$−I and Ag$^0$−I differentials include a peak at ∼2.89 Å corresponding to the first shell Ag−I distance between tetrahedrally coordinated Ag$^+$/I$^-$. For the Ag$^+$−I, there are no distinct features in the $d$-PDF beyond ∼7 Å suggesting a subnanometer structure.

This differential was best fit by an α-AgI model[24] with peaks up to ∼7 Å. This is in contrast to the Ag$^0$I, in which the high-$r$ data ($r > 15$ Å) could be fit by the γ-AgI phase alone (with ∼3 nm particles), but whose low-$r$ region indicated the existence of a second AgI-phase with finite particle size. The low-$r$ residual from the single phase fit was consistent with α-AgI. By including an α-AgI phase with peaks up to 7 Å a good fit to the data was obtained. For both the silver-exchanged and reduced silver MOR, the length scale of the α-AgI clusters (7 Å) is consistent with the confinement of α-AgI within the MOR pores (Figure 3). The absence of clear correlations associated with cluster−zeolite interactions suggests that the clusters are not crystallographically ordered within the zeolite lattice.[25]

The stabilization of the high temperature α-AgI phase at low temperature occurs through a different mechanism than previously documented. Smaller α-AgI particles have been known to reduce the α-to-γ/β transition temperature with cooling, such that following the γ/β-to-α transition (>147 °C) the α-phase is retained to lower temperature. Here, the AgI-containing zeolite is never heated above 147 °C and yet the α-AgI phase is formed, probably via a direct route. The subnanometer clusters are the smallest AgI particles characterized to date that share the structure of the bulk material. More typically, clusters of this length scale have formed with well-

defined compositions and connectivities unrelated to the bulk (stabilized by cluster−zeolite interactions or large capping ligands, e.g., the cube-like $Ag_4I_4$).[25,26] The AgI particles are much smaller than those studied previously ($\sim$10−100 nm)[12] and persist to the lowest temperature yet documented—at least room temperature. Particles of this size would be "diffraction amorphous" and difficult to characterize without using PDF methods. Indeed, while the highly penetrating high energy X-rays used for PDF measurements minimize beam damage, volatility of the sample in the electron beam prevented reliable TEM imaging of these systems.
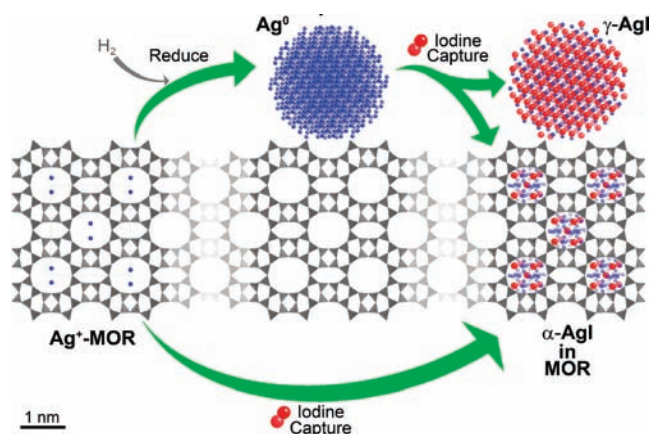


**Figure 3.** A schematic of iodine capture by silver-containing MOR. While prereducing the silver MOR yields in a mixture of $\gamma$-AgI nanoparticles and subnanometer $\alpha$-AgI, direct iodine uptake by silver-exchanged MOR produces exclusively subnanometer $\alpha$-AgI.

In conclusion, using a differential approach to PDF analysis we have shown that the structure and distribution of the AgI formed when iodine is captured by silver-containing MOR depends on whether the silver is reduced. It is intriguing that two different forms of the AgI exist when prepared from reduced silver-exchanged MOR ($Ag^0$-MOR). While the reduced $Ag^0$ exists as a single phase with $\sim$3 nm particles on the zeolite surface, upon $I_2$-treatment two AgI phases are formed—subnanoscale $\alpha$-AgI within the pores and larger $\gamma$-AgI nanoparticles on the zeolite surface (Figure 3). This would imply that material migrates into the zeolite pores during the $I_2$-treatment. This may be enabled by the combined mobility of the $I_2$ molecules, initially physisorbed into the pores, the mobility of the $Ag^0$ atoms on the zeolite surface, and the mobility of the $Ag^+$ ions within the $\alpha$-AgI structure.

For the unreduced silver-exchanged MOR, the AgI is confined to the pores as subnanometer $\alpha$-AgI clusters. Encouragingly, this may represent a more secure route for radioactive iodine capture, with the possibility of using pore-blocking to further trap the iodine for long-term storage.

Separate to the relevance of these materials for radiological gas capture and long-term storage, the data also provide exciting new possibilities in the field of nanoscaled ionic conductors. Previous studies have shown that the progressive reduction in AgI particle size toward the nanoscale not only stabilizes the superionic $\alpha$-phase but also produces orders of magnitude enhancement in the ionic conductivity. The subnanometer particles documented here may yield further large gains in conductivity.

Ongoing research efforts are focusing on better understanding the structure−property relationship of porous crystalline materials for radiological iodine capture. This includes studies on other zeolitic systems and appropriate metal−organic frameworks, lower concentrations of $I_2$ approaching the trace levels found in waste streams, exploring phase behavior of the 7 Å AgI clusters, probing the redox chemistry underlying $I_2$ capture in unreduced silver-exchange systems, and directly monitoring the $I_2$-sorption and AgI formation through *in situ* time-resolved PDF studies.

**Supporting Information Available:** Details of sample preparation and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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