



# Silver-mordenite for radiologic gas capture from complex streams: Dual catalytic CH<sub>3</sub>I decomposition and I confinement



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## ABSTRACT

The selective capture of radiological iodine (<sup>129</sup>I) is a persistent concern for safe nuclear energy. In nuclear fuel reprocessing scenarios, the gas streams to be treated are extremely complex, containing several distinct iodine-containing molecules amongst a large variety of other species. Silver-containing mordenite (MOR) is a longstanding benchmark for radioiodine capture, reacting with molecular iodine (I<sub>2</sub>) to form AgI. However the mechanisms for organoiodine capture is not well understood. Here we investigate the capture of methyl iodide from complex mixed gas streams by combining chemical analysis of the effluent gas stream with in depth characterization of the recovered sorbent. Tools applied include infrared spectroscopy, thermogravimetric analysis with mass spectrometry, micro X-ray fluorescence, powder X-ray diffraction analysis, and pair distribution function analysis. The MOR zeolite catalyzes decomposition of the methyl iodide through formation of surface methoxy species (SMS), which subsequently reacts with water in the mixed gas stream to form methanol, and with methanol to form dimethyl ether, which are both detected downstream in the effluent. The liberated iodine reacts with Ag in the MOR pore to the form subnanometer AgI clusters, smaller than the MOR pores, suggesting that the iodine is both physically and chemically confined within the zeolite.

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## 1. Introduction

Effective management of radionuclides is critical to safe nuclear energy. Amongst the various radionuclides, several are considered to be “volatile”, including <sup>129</sup>I, <sup>3</sup>H, <sup>14</sup>C, and noble gases (largely isotopes of Kr and Xe). These must be selectively captured from gas streams for long term storage [1]. In contrast to conventional gas (e.g., CO<sub>2</sub>) capture applications, which target an individual molecular species within a mixed gas stream, in processing nuclear effluent, the targeted radionuclides are often part of several distinct molecules. Consequently multi-functional sorbent materials are needed to selectively capture several chemically-distinct species from a complex mixed gas stream.

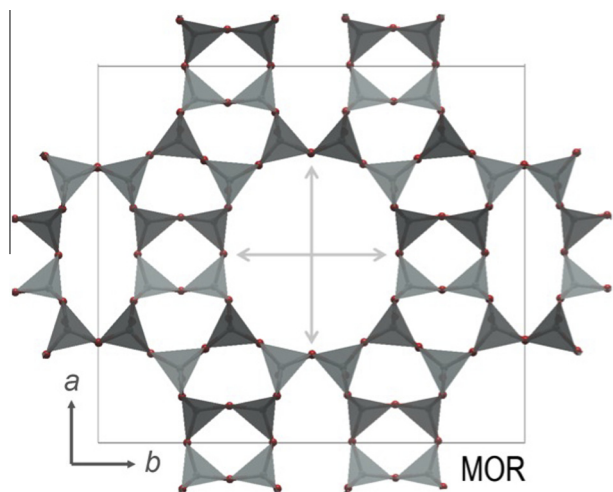
<sup>129</sup>I is a volatile radionuclide that remains a concern. While this radionuclide is only found in small concentrations in

nuclear effluent, where it exists as H<sup>129</sup>I, <sup>129</sup>I<sub>2</sub>, and/or organoiodides, its long half-life (~10<sup>7</sup> years) and its involvement in human metabolic processes means that the effective capture of iodine is important for public safety [2].

The leading approach to capture radioactive iodines during nuclear fuel reprocessing involves sorption onto silver-containing zeolites. For many decades the silver-exchanged zeolite mordenite, (Ca,Na<sub>2</sub>,K<sub>2</sub>)Al<sub>2</sub>Si<sub>10</sub>O<sub>24</sub>·7H<sub>2</sub>O, (MOR, Fig. 1) has been the zeolite-of-choice for radioactive iodine capture due to its high Si:Al ratio which enhances stability in the acidic waste streams and allows for relatively high Ag-loadings. The MOR framework structure [3] is comprised of 12 membered rings (7.0 × 6.5 Å) and 8 membered rings (5.7 × 2.6 Å) parallel to the crystallographic *c*-axis, and another set of 8 membered rings parallel to the crystallographic *b*-axis (3.4 × 4.8 Å). Due to the configuration of the pore system, MOR is defined as containing only a one-dimensional diffusion channel for large extraframework ions or molecules. Until recently, the molecular basis for its performance had remained largely unexplored [4,5]. We have successfully undertaken studies to probe the structure of Ag-MOR, [6] and how it captures gaseous I<sub>2</sub> as supported AgI nanoparticles and clusters [7]. These studies

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**Fig. 1.** The MOR structure. The MOR framework defines one-dimensional channels (12-rings,  $6.5 \times 7.0$  Å) parallel to the *c*-axis which contain the exchangeable cations and water molecules (omitted for clarity) [48]; general composition:  $(X^{+})_2AlSi_{10}O_{24}$ .

have been extended to the capture of  $I_2$  gas by a variety of porous crystalline materials (including zeolites and metal–organic frameworks (MOFs)), [7–10] the storage of the iodine gas in durable waste forms [11,12], and the combined storage/capture of iodate and iodides from caustic aqueous streams [13]. Worldwide, a larger effort for the capture and storage of iodine is underway. Additional capture strategies include  $I_2$  gas with silver-impregnated amorphous silica [14], chalcogen-based aerogels [15,16], and MOFs for the extraction of  $I_2$  from organic solutions [17]; additional storage strategies include the incorporation of iodine in structurally compatible apatite mineral analogs [18,19] and iodine immobilization via hot isostatic pressing [20].

With the complex off-gas effluent streams and the potential for competitive adsorption, we are extending our investigation of silver-mordenite as an iodine capture material to other iodine-containing molecules. In particular, we explore the interaction of an organoiodide, methyl iodide ( $CH_3-I$ ), with Ag-MOR. In addition to  $CH_3-^{129}I$  being a radiological by-product of nuclear fuel reprocessing, [21] methyl iodide is a known pesticide [22] and chemical methylating reagent, [23] including in the methanol-to-gasoline (MTG) catalytic process [24]. Optimization of these catalytic processes also benefits from understanding the interactions with  $CH_3-I$  and its adsorption properties.

It is a standard practice to reduce the  $Ag^+$ -exchanged MOR prior to use. Here, the capture of  $CH_3-I$  from a complex acidic stream by a reduced silver MOR is investigated. Significant complexity of the organic iodide- (guest-) loaded Ag-MOR host contributes to the challenge in decoupling the guest structure and framework distortion of the host lattice. Therefore, to develop an understanding of the structure–function relationship, a combined experimental approach was necessary. This includes infrared (IR) spectroscopy, thermogravimetric analysis (TGA) with mass spectrometry (MS), micro-X-ray fluorescence ( $\mu$ -XRF), powder X-ray diffraction (XRD) analysis, and pair distribution function (PDF) analysis. We apply a differential approach to pair distribution function (d-PDF) analysis. The PDF method probes the local structure of nano-scale 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 [25] it is possible to isolate contributions from individual components within a material [26]. This differential

approach 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.

## 2. Experimental

### 2.1. $CH_3-I$ loaded $Ag^{\circ}$ -MOR

The Ag-MOR is IONEX Type Ag 900 E16 (manufactured by Molecular Products using UOP AW-300 Mordenite). It is a silver-exchanged natural mordenite zeolite in the form of extruded pellets (1/16 in.; 3–6 mm  $\times$   $\sim$ 3 mm diameter), that was heated at 150 °C under  $H_2$  flow (3% in  $N_2$ ) for ca. 12 h to reduce the  $Ag^+$  to the metallic state. The resulting material, MOR-supported metallic  $Ag^{\circ}$  ( $Ag^{\circ}$ -MOR), has an approximate formula of  $(Ag,H^+)_{1.52}Fe_{0.10}Ca_{0.11}K_{0.16}Al_2Si_{10}O_{24} \cdot 4H_2O$ , with charge-balancing protons ( $H^+$ ) from the reducing  $H_2$  stream [27,28].

#### 2.1.1. Static adsorption experiments

A ceramic boat containing  $Ag^{\circ}$ -MOR was heated at 150 °C in a tube furnace. A  $CH_3-I$  vapor in  $N_2$  carrier gas, flowing at  $\sim$ 2 ml/min, was passed over the zeolite for 24 h. Unadsorbed excess  $CH_3-I$  was captured in a water bath outside the tube furnace. Based on the mass gain in the recovered sample, suggested a loading of 8.5 wt% I on the Ag-MOR. The color of the exposed MOR sample lightened from dark gray to yellowish-gray.

#### 2.1.2. Deep bed iodine sorbent test experiments

(Fig. 2) Approximately 10 g of  $Ag^{\circ}$ -MOR was loaded into a vertical sorption bed column (1.9 cm diameter, and up to 20 cm length) located within a temperature-controlled oven set at 150 °C. The inlet mixed gas stream composition was approximately (by volume) 18,000 ppm (1.8%) water vapor, 800 ppm  $NO$ , 800 ppm  $NO_2$ , and 57 ppm  $CH_3I$  in air, with a flow rate of 0.73 L/min [29]. Sorption was undertaken over a ca. 1 month period monitoring the effluent gas stream using gas chromatography for methyl iodide and organic byproduct species, and using gas absorption in 0.1 N NaOH followed by inductively-coupled plasma mass spectroscopy (ICP-MS) for inorganic iodine species  $I_2$  and HI. Loading of iodine on separate sorbent bed segments was determined gravimetrically and confirmed using the measurements of the  $CH_3I$  and  $I_2$ /HI remaining in the gas between each bed segment. Additional information on iodine breakthrough is provided in the [Supplementary data](#).

### 2.2. Gas chromatography-flame ionization detector (GC-FID)

Gaseous methyl iodide concentrations were measured using a gas chromatograph (GC; Hewlett Packard 5890 GC) with a flame ionization detector (FID). Gas samples can be injected into the GC using a sample loop, syringes, or solid-phase micro-extraction (SPME) syringes, which improve the methyl iodide detection limit by approximately 100 $\times$  to approximately 10 ppb.

### 2.3. Inductively coupled plasma-mass spectrometry (ICP-MS)

The ICP-MS is a Thermo Series II – CCT inductively coupled plasma quadrupole mass spectrometer with a Cetac 520 autosampler equipped with a Teflon lined carbon fiber sample probe. The sample introduction system is hydrofluoric acid compatible, made by ESI. It consists of a 100  $\mu$ l/min PFA nebulizer and PFA Scott spray chamber. The torch is quartz with a demountable sapphire injector. Sample and skimmer cones used for the torch interface are nickel with platinum orifice inserts. The use of PFA/HF

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