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Determine Mechanism of CH_3I Capture in AgZ

Fuel Cycle Research & Development

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Prepared for
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Separations Working Group

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Determine Mechanism of CH_3I capture in AgZ:

Silver-mordenite for radiologic gas capture from complex streams - Dual catalytic CH_3I decomposition and I confinement

Fuel Cycle Research & Development

Prepared for
U.S. Department of Energy
Separations and Waste Forms

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SUMMARY

The selective capture of radiological iodine (^{129}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_2) 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. 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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ABBREVIATIONS AND ACRONYMS

Å	Angstrom
AgI	Silver Iodine
Al	Aluminum
APS/ANL	Advanced Photon Source / Argonne National Laboratory
°C	Degrees Celsius
CH_3I	Methyl iodide
cm	Centimeter
d	diameter
d-PDF	differential- Pair Distribution Function analysis
FCRD	Fuel Cycle Research and Development
GCM	Glass Composite Materials (waste form)
GC-FID	Gas chromatography-flame ionization detector
INL	Idaho National Laboratory
I_2	Iodine (gas)
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
INL	Idaho National Laboratory
IR	Infrared Spectroscopy
µ	Micro
M	mole/liter
MOR	Mordenite Zeolite
O	Oxygen
Si	Silicon
SMS	Surface Methoxy Species
SNL	Sandia National Laboratories
XRD	X-ray Diffraction
XRF	Micro-X-ray fluorescence

1. INTRODUCTION

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, $(Ca,Na_2,K_2)Al_2Si_{10}O_{24}{\bullet}7H_2O$, (MOR) 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 is comprised of 12 membered rings (7.0 x 6.5 Å) and 8 membered rings (5.7 x 2.6 Å) parallel to the crystallographic c-axis, and another set of 8 membered rings parallel to the crystallographic b-axis (3.4 x 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.[1,2]

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.

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 (μ-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[3] it is possible to isolate contributions from individual components within a material.[4] 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 METHODS

2.1. CH_3-I loaded Ag°-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 (1/16in.; 3–6mm x ~3mm diameter), that was heated at 150°C under H_2 flow (3% in N_2) for ca. 12h to reduce the Ag^+ to the metallic state. The resulting material, MOR-supported metallic Ag° (Ag°-MOR), has an approximate formula of $(Ag,H^+)_{1.5}Fe_{0.10}Ca_{0.11}K_{0.16}Al_2Si_{10}O_{24}{\bullet}4H_2O$, with charge-balancing protons (H^+) from the reducing H_2

stream.[5,6]

2.1.1. Static adsorption experiments

A ceramic boat containing Ag°-MOR was heated at 150 °C in a tube furnace. A CH_3-I vapor in N_2 carrier gas, flowing at ~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

Figure 1. Approximately 10 g of Ag°-MOR was loaded into a vertical sorption bed column (1.9cm diameter, and up to 20cm 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.[7] 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.

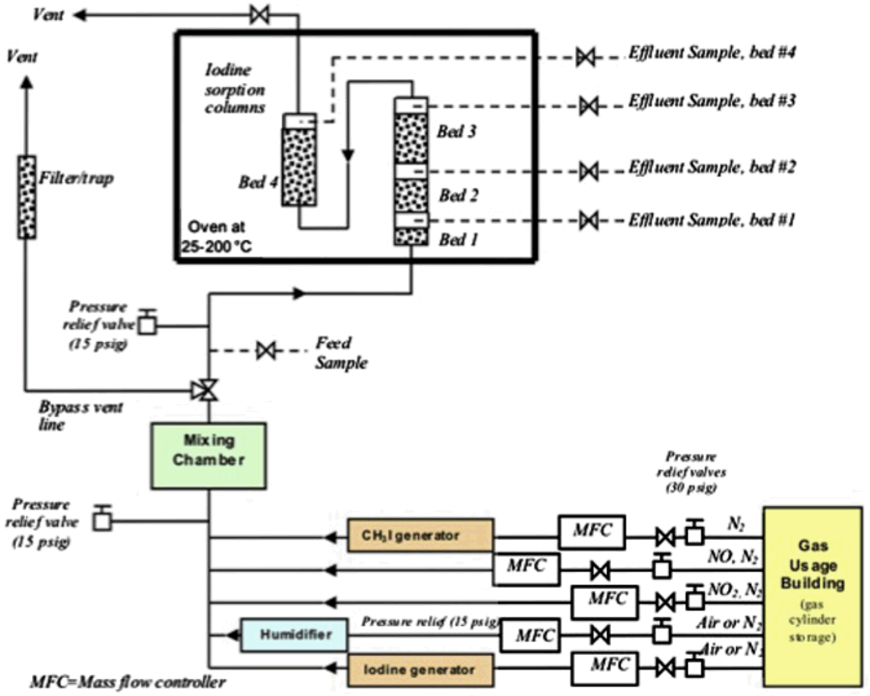

Figure 1: Iodine sorbent deep bed test system used in the capture of iodine from a complex stream containing CH_3I, H_2O, NO and NO_2 with a carrier gas of air.

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 100x 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 μl/min PFA nebulizer and PFA Scott style 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 compatible components minimizes the instrument memory effect for iodide.

2.4. High-energy synchrotron X-ray scattering analysis

High energy X-ray scattering data for the deep bed sorption test materials loaded in polyimide capillaries were collected at beamline 11-ID-B at the Advanced Photon Source at Argonne National Laboratory. Total scattering data suitable for PDF analysis were collected at ~87 keV, k = 0.1430 Å for the sample recovered from the sorption experiment and at ~90 keV, k = 0.1370 Å for unreduced Ag^+-MOR (for the reference PDF) and the pristine Ag°-MOR sample used for sorption experiment. A large amorphous silicon-based area detector was used to record two-dimensional diffraction images.[8,9] These data were reduced to one-dimensional scattering data within fit2d.[10]

2.4.1. Pair distribution function (PDF) analysis. The PDFs, G(r), were obtained from the total scattering data, collected to high values of momentum transfer, $Q_{max} = 20$ Å^{-1}, using PDFgetX2.[11] Contributions from the background, Compton scattering, fluorescence, to the total scattering data were subtracted. Differential PDFs (d-PDFs) which isolate the correlations involving the species within the zeolite pores were recovered by subtracting the PDF for the unreduced Ag^+-MOR as described previously.[12] Structural models were refined against the d-PDFs within PDFgui.[13] The intensities of selected peaks were quantified by fitting Gaussian functions within fityk.[14]

2.5. Thermogravimetric analysis-differential scanning calorimetry (TGA–DSC) and mass spectrometry (MS) analyses

The thermal desorption of guests and eventual framework decomposition was investigated by TGA–DSC–MS. Measurements used a SDTQ600 TA instrument, equipped with a mass-spectrometer gas analyzer MS-ThermoStar from Pfeiffer Vacuum. Samples were heated at 10 °C/min to 800 °C under helium flow.

2.6. Micro-X-ray fluorescence (μ-XRF)

The μ-XRF analysis was performed using a Bruker M4 Tornado μ-XRF mapping system. The instrument was equipped with a micro-focused Rh source (50kV, 600μA) with a poly-capillary optic (~30 μm spot-size). Fluorescence spectra were collected using two silicon-drift detectors. Powder specimens were loaded in small Teflon cups (~2 mm inner diameter), then secured to the xy-translation stage within the M4, and XRF spectra were collected under vacuum (~10^{-3} Torr). Quantification of the elements (Si, Al, Ag, I, Ca, Mn, and Ca) used the “Quantitative analysis” routines within the M4 software. These measurements were uncalibrated, so only relative changes in elemental abundances or approximate elemental absolute abundances are provided.

2.7. Infrared spectroscopy (IR)

IR spectra were collected on a Thermo Scientific Nicolet iS10 Smart iTR in transmission geometry. Samples are sub-milligram in size. Spectra collected in air, in the range 3500 – 500 cm^{-1}.

3. RESULTS & DISCUSSIOM

Initial static adsorption testing and ICP-MS studies were used to calculate an approximate stoichiometric formula for the Ag°-MOR (natural) sample that is exposed to CH_3-I: $(AgI)_{1.02}$ $(H_{1.54}K_{0.16}Ca_{0.10}\ Fe_{0.05}Al_2Si_{10}O_{24})$ with residual Ag = 0.42. Note, this is a bulk calculation of an inhomogeneous material. This material was used as the sorbent in the deep bed testing experiments.

In these subsequent experiments, several different organic compounds were initially detected in the effluent gas stream. They included dimethyl ether (DME), methyl nitrite, and methanol. This observation is generally consistent with earlier studies: Haefner[15] observed methanol in the off-gas, and Scheele[16] proposed that methanol and DME observed in the off-gas are organic byproducts from methyl iodide adsorption on Ag-MOR.

As the sorption column approached breakthrough, the sorption process slowed, and the outlet effluent gas composition approached that of inlet gas with added organic compounds including DME and methanol. Quantitative analysis of the effluent gas stream indicates that not all of the organic methyl component from the methyl iodide can be accounted for by the organic byproducts detected in the effluent stream. This observation suggests that some of the organic component may remain adsorbed on the sorbent or may be converted into other gaseous byproducts (e.g., CO, CO_2, H_2O and/or H_2).

After column breakthrough, non-organic iodine-containing species (either I_2 or HI) are also detected downstream of the sorbent beds, indicating that methyl iodide is decomposed and converted to other species through interactions with Ag-MOR, independent of the iodine capture itself. This is consistent with earlier studies[15,16]: after breakthrough occurs, a significant portion (10 to >90%, depending on degree of breakthrough) of iodine that passes through the zeolite bed exists as either I_2 or HI, but not the original methyl iodide.

The mass gain for the Ag°-MOR sorbent attained at saturation for the deep bed sorption testing, suggests that iodine is loaded at a ca. 5.2 wt% level. This corresponds to ~55% utilization of silver-loaded within MOR zeolite (presuming I is confined as AgI) – a relatively high level of

Ag-utilization. This represents an upper estimate for the iodine-loading as some of the weight gain may be associated with adsorption of species from the input gas stream or generated in situ through interactions with the sorbent (e.g., CH_3I, H_2O, or NO_x). Refinement of a structural model against the d-PDF of Ag°-MOR prior to CH_3I exposure (using a spherical particle diameter parameter to model the attenuation of peaks in the PDF at high r) indicates that the sample consists of 8 nm Ag nanoparticles with a face-centered cubic structure (a = 4.078 Å, R ~13.4%) supported on MOR. By contrast, the d-PDF for the post-sorption, CH_3I-treated system was dominated by features at short distance, below ca. 6 Å. Refinements of models against the data within PDFgui, suggested that these were predominately subnanometer clusters of an AgI phase (likely α-AgI) with a minor component of larger γ-AgI nanoparticles (11%, ca. 6 nm). The structural models for the AgI phases were based on those previously reported for I_2-treated synthetic Ag-MOR systems. [12] In the case of the subnanometer α-AgI clusters, these only contribute features to the PDF below ~7 Å (~6–8 atoms) corresponding to the nearest- and next-nearest-neighbor Ag-I and I-I distances. Based on earlier in-depth studies of the mechanism of supported particle formation in MOR,[17] such clusters are likely confined within the 12-member ring MOR channels. The largest deviation in the fit of the AgI phases to the data is apparent for the feature(s) at 2.7– 3.0 Å which corresponds to the nearest-neighbor Ag-I distance. While the overall intensity of this feature is well modeled by the AgI phase, it appears to contain contributions from two distinct peaks with similar distances. These peaks are centered at 2.77 Å and 2.97 Å, with relative peak areas of 3:1. These distinct distances may reflect local defects/distortions in the α-AgI phase.

There was no evidence for residual face-centered cubic metallic Ag°, suggesting that either the Ag° has been fully reacted to form AgI or that the Ag° is completely re-oxidized during the on-stream sorption process. Given the distribution of the subnanometer AgI clusters versus larger AgI nanoparticles observed here, and our previous studies that indicate that subnanometer AgI clusters are the more heavily produced when iodine (albeit as I_2, not CH_3I) is captured by unreduced Ag^+-MOR, we propose that a degree of reduction of the supported Ag^+ ion to Ag° metal likely occurs in situ/online.

The thermal analyses (TGA–DSC–MS; see Figure 2) provide insight into adsorbed species, including the stability regime of the confined iodine. In the TGA, a ~0.5 wt% weight loss at 100 °C and ~2.5 wt% loss centered at ~150 °C are associated with H_2O and CO_2 loss. In the DSC, an endothermic peak at 152 °C is attributed to α-AgI temperature-induced phase transition for the MOR-supported γ-AgI[12] (ambient mixtures of the β- and γ-AgI polymorphs transform to the α-phase above 147 °C).[18-21] There is a general exothermic slope matching a TGA weight loss seen at ~225 °C.

The thermal events can be identified based on insights from the simultaneous MS analysis. Below 100 °C, there is loss of CO_2 that is presumably excess SMS-related organic at the bulk surface of the zeolites. Near 160 °C, a combination of CO_2, H_2O/OH are released; this corresponds to occluded and/or pore adsorbed water and organic molecules.[24] At ~225 °C, iodine (I) and CO release commences, while CO_2 exhibits continuous weigh loss from this temperature. The O_2 and CO weigh loss progressively increases to maximal values at 600 °C, suggesting that they are continuously off gassing due to heating above 225 °C. There is no evidence of AgI, NO_2, or I_2 loss in the temperature range studied.

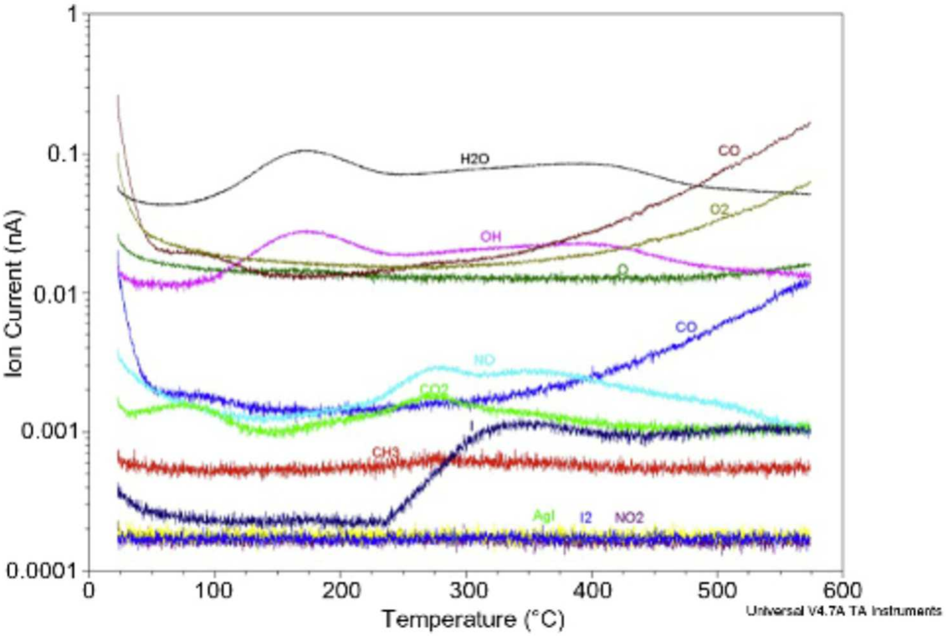

Figure 2: Mass Spec data from simultaneous TGA-DSC-MS, run under flowing He of AgI-MOR after iodine sorption from the complex stream.

As expected, the XRF analysis of the CH_3I-Ag-MOR loaded samples detects Ag, Ca and Fe, with Ca and Fe in lower molar fractions than Ag. This is confirmation of incomplete ion exchange of the silver for the naturally-occurring charge balancing cations. Post thermal treatment XRF data confirms that AgI is not lost to volatilization above its melting point of 556 °C, but instead is retained as AgI nanoparticles inside the MOR pores. Both analyses also confirm excess silver in the samples. This information combined with the lack of AgI melting in the TGA/DSC is confirmation of in-pore confinement of sub-nanometer nanoparticles of AgI,[12] and of added stability and retention of the AgI at higher temperatures.

The IR spectra for the as-received Ag°-MOR and the CH_3I-exposured CH_3I-Ag°-MOR show minimal changes. The absence of any new IR features associated with surface methoxy species on the recovered MOR samples supports the results of the X-ray structural analyses. The data shows no evidence for persistent organic functionalization of the zeolite framework i.e. Al/ Si(–O–)C peaks) and no direct long-term capture of CH_3I species in the pores of the MOR (as a possible functionalized silver nanoparticle).

Discussion.

These experiments were performed under simulated industrial conditions of fission off-gas capture for nuclear fuel reprocessing. This is based on the naturally-occurring zeolite in a bulk pelletized form (during both the prior reduction and packed into the sorption beds). Accordingly, not only does the zeolite sorbent include complex defects in the crystal structure and a distribution of different charge compensating cations (Ca^{2+}, K^+, presumably H^+ and residual Ag^+) in the pores, but these are likely to be in homogeneously distributed throughout the sorbent pellets. Thus on a local scale, several different zeolite micro-environments, including basic (Ag^+, Ca^{2+}, K^+) and acidic (Ag° and H^+) in nature may contribute to the organoiodine confinement.

The capture of iodine from organoiodines such as CH_3I by Ag- MOR proceeds via a series of catalytic and sorption processes. The extensive research into the catalytic properties of zeolites and the associated mechanistic understanding can be applied to inform our understanding of the present organoiodine capture processes. Specifically, the formation of alkoxy species on the zeolite surface, such as ***surface methoxy species*** (**SMS**, Al– O(Me)–Si), is known to be a key intermediate in a number of important catalytic processes, including methanol-to-gasoline (MTG) conversion.

The SMS, formed by addition of the methyl halides, can react with a number of different molecules in the stream to form various hydrocarbon products. For example, SMS reacts with water to form methanol, and methanol to form DME in each case regenerating the acid site. The SMS can react with NO_x to form methyl nitrite leaving a basic site. Reaction with O_2, and oxidation of the SMS produces CO and CO_2.[22]

Based on the species observed downstream from the CH_3I adsorption over the Ag-MOR, the TGA/DSC–MS of the iodine loaded AgI-MOR and the structural analyses, we postulate the following reactions occur in the process of capturing the iodine from the complex input stream of CH_3I, H_2O, NO, NO_2 and air. First, CH_3I is cleaved to form an iodine species and a SMS at the low operating temperature of the adsorption process, 150 °C. Second, the iodine reacts with the Ag to form AgI nanoparticles inside the zeolite pore. Third, the SMS react with NO_x to form methyl nitrite or with water to form methanol which can further react with other SMS to form dimethyl ether. Methanol, dimethyl ether and methyl nitrite are observed downstream of the adsorption column. This is shown schematically in Figure 3.

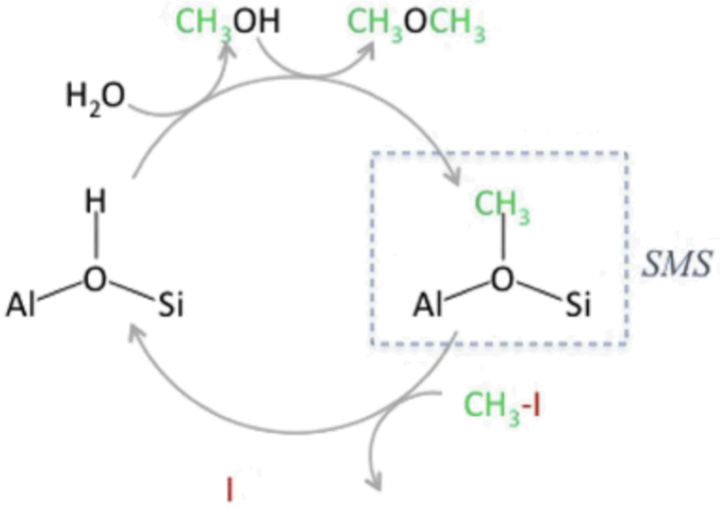

Figure 3: A schematic portraying the dual catalytic CH_3I decomposition and I confinement reaction pathway over the Ag°-MOR zeolite framework (-Si-O(-H)-Al-). The SMS unit is identified. Note: the fate of the charge balancing proton is not fully elucidated.

The TGA–DSC–MS data of the final iodine adsorbed zeolite indicates that at 225 °C, there is a release of iodine, NO, CO and CO_2 species from the sample. The NO is probably desorbing from the zeolite pore as they are readily adsorbed by acidified aluminosilicate zeolites, including MOR.[26] We postulate that CO and CO_2 are produced by the oxidation of excess and/or residual SMS on the zeolite, through reactions with sorbed H_2O or nitrites.

There is no evidence of AgI loss (melting point 556 °C) up to 600 °C. Instead, it appears that the AgI is forming the sub-nanometer α-AgI clusters in the zeolite pores and have been identified previously in the literature;[12] these clusters are too small to produce Bragg peaks and therefore cannot be identified by powder X-ray diffraction. This has been confirmed by the XRF data that identifies Ag and I in similar ratios in the pre- and post-heated (600 °C) CH_3I-Ag-MOR samples.

Interestingly, the resultant AgI-MOR product after CH_3I interactions, appears to be a less stable iodine capture material that that formed from the adsorption of pure I_2 gas on the same as-received starting material Ag°-MOR (natural) to form AgI-MOR (I loss begins at approximately 360 °C). Examination of the data leads to the conclusion that the desorption of NO and CO may be facilitating the loss of excess I (acidified, and in the form of HI) from the pores and bulk surface of the mordenite.

4. CONCLUSIONS

A full detailed accounting of this study, with detailed descriptions of all sorption and materials characterization data, is in a recently published manuscript.[23]

The CH_3I is catalytically cleaved over the partially reduced Ag°- mordenite natural zeolite. In that cleaving process, surface methoxy species are formed at the mordenite acid sites; the iodine species is either captured by the silver to form occluded AgI in the MOR pores, or it reacts to form unbound I_2 or HI. There is evidence of nitrite species also being adsorbed from the inlet gas stream on the mordenite. As the reaction proceeds, the SMS react to form a number of off-gas species such as methanol, dimethyl ether, and methyl nitrite.

The combination of chemical, thermal and mechanical stability of the zeolites make them strong candidates for the use in nuclear energy applications. The chemical and physical confinement of the radiological species (e.g., $Ag^{129}I$) inside the pores of the zeolite allows for the safe manipulation of the material into a waste form for long-term decay storage. Durability studies into the incorporation of iodine captured from complex streams into waste forms that are chemically durable (e.g., SNL low temperature sintering Bi–Si oxide glass)[24] for a variety of postulated repository geologies, indicated that releases of Ag and I at the same low rates as I_2-loaded AgI-MOR Glass Composite Material (GCM) waste form, and by the same mechanism.[25]

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