Proceedings of Global 2015
September 20-24, 2015 - Paris (France)
SAND2015-1943C

SILVER-MORDENITE FOR RADIOLOGIC GAS CAPTURE FROM COMPLEX STREAMS: DUAL CATALYTIC CH3I DECOMPOSITION AND I CONFINEMENT

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Abstract – 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. Herein we investigate the capture of methyl iodide (CH_3-I) 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.

I. 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 successfully explored the interaction of an organoiodide, methyl iodide (CH_3-I), with Ag-MOR.[3]

II. EXPERIMENTAL METHODS

Deep bed adsorption studies were combined with materials characterization and structural analysis methods in an effort to fully understand the structure-property relationship between the Ag-MOR and the capture of iodine from organo-iodide species in complex streams.

II.A. CH_3-I loaded Ag°-MOR

The Ag-MOR is IONEX Type Ag 900 E16 (manufactured by Molecular Products using UOP AW-300 Mordenite); 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 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]

II.B. Deep Bed Iodine Sorbent Test Experiments

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. Sorption was undertaken over ca. 1 month 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, HI.

II.B. Materials Characterization Methods

The following techniques were used to characterize the materials in this study: Gas chromatography-flame ionization detector (GC-FID); Inductively coupled plasma-mass spectrometry (ICP-MS); Thermogravimetric analysis - differential scanning calorimetry (TGA–DSC) and mass spectrometry (MS) analyses; Micro-X-ray fluorescence (μ-XRF); Infrared spectroscopy (IR).

II.C. Structure 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. Pair distribution function (PDF) analysis (PDF) and Differential PDFs (d-PDFs) were used to study both the zeolite and the species within the zeolite pores.

III. RESULTS AND DISCUSSION

Based on our observable data, 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. CH_3I is cleaved to form an iodine species and a Surface Methoxy Species (SMS) is formed on the zeolite. The iodine reacts with the Ag to form AgI nanoparticles inside the zeolite pore. 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. See Figure 1.

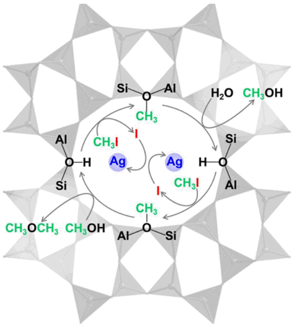

Fig. 1. Schematic of catalytic cleaving of CH_3-I and iodine capture by Ag°-MOR.

Thermal analyses 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. 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.

IV. CONCLUSIONS

The CH_3-I is catalytically cleaved over the partially reduced Ag°-mordenite natural zeolite. The organic components react with the zeolite and are eventually isolated downstream. 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. 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.

ACKNOWLEDGMENTS

This research was supported by the U.S. DOE/NE/FCRD-SWG. Sandia National Laboratories is a multiprogram laboratory managed & operated by Sandia Corp., a wholly owned subsidiary of Lockheed Martin Corp., for the U.S. DOE’s NNSA, under Contract No. DE-AC04-94AL85000. Work done at Argonne and use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. DOE/Office of Science by Argonne National Laboratory, was supported by the USDOE, Contract No. DE-AC02-06CH11357. The Idaho National Laboratory is a U.S. Department of Energy National Laboratory operated by Battelle Energy Alliance, for the U.S. Department of Energy, Office of Nuclear Energy, under DOE Idaho Operations Office Contract DE-AC07-05ID14517.

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