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Studies on the Mechanisms of Methyl Iodide Adsorption and Iodine Retention on Silver-Mordenite

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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 are 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.

Results indicate that the capture of iodine CH_3I by Ag- MOR proceeds via a series of catalytic and sorption 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. 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 dimethyl ether (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.[1]

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.[2,3] 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 seen downstream of the adsorption column. See Figure 1.

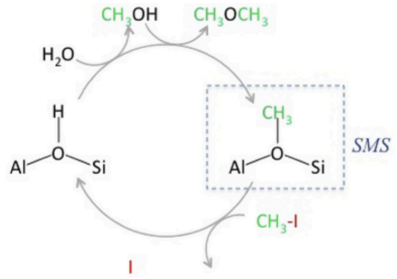

Figure 1: A schematic portraying the dual catalytic CH_3I decomposition and I confine ment reaction pathway over the Ag°-MOR zeolite framework (-Si-O(-H)-Al-). The SMS unit is identified. Note: the fate of the charge balancing proton is not fully elucidated.

Iodine Retention during Waste Form Preparation.

Evaluations were performed on how the iodine adsorbed from CH_3-I is retained during waste form production. Thermal data of the loaded MOR indicates that at 225 °C, there is a release of iodine, NO, CO and CO_2. We postulate the NO is desorbing from the pore,[4] and CO/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.[5] 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.

Excess I (as HI or I_2) that was not captured by the pore-occluded Ag, is released at a

lower temperature (~250°C) than pure I_2 captured by Ag-MOR (I loss begins at approximately 360 °C). Examination of the data suggests that NO and CO desorption may be facilitating the loss of excess I from the pores and bulk surface of the mordenite.

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