

Changes of Iodines on Platinum Catalyst Used as Hydrogen Mitigation

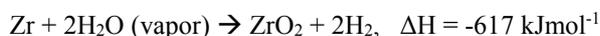
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1. Introduction

Hydrogen explosions occurred during the accidents of nuclear power plants (NPPs) such as in Three Mile Island (TMI in 1979) and Fukushima (in 2011) owing to a large quantity of hydrogen generation from interactions between the core melt with containment structures and water. For example, a molten core (corium) reaction with concrete and an oxidation reaction between oxygen (O_2) of a high-temperature steam (H_2O) and zirconium (Zr) cladding can lead to the production of H_2 :



However, water radiolysis and corrosion of metals (such as zinc, alumina, or iron) can also produce hydrogen in water-cooled nuclear reactors, even during normal operations. As a result, hydrogen combustion is a real threat that must be mitigated.

Pt catalysts based on alumina (Pt/Al_2O_3) are commonly used for the oxidation of H_2 . However, the catalytic recombiner performances are known to decrease, perhaps as a result of the poisoning on the surfaces of the passive autocatalytic recombiner (PAR). We are particularly interested in iodine poisoning, so various iodine species were applied on Pt/Al_2O_3 to investigate changes of the iodines on Pt/Al_2O_3 .

2. Experiment Details

2.1 Iodine cycle in containment building

As can be seen in the gaseous forms (shown in pink-filled circle) of iodine in Figure 1, it was reported that IO_x could be produced owing to the oxidation of I_2 (and organic iodine, RI, too) by the radiolytic products of air (such as NO_2 , O_3 or HNO_3) in the containment building of NPPs, even though the IO_x partially decomposes back to I_2 and RI under irradiation. The produced IO_x can take up water (on the surface of the catalyst as used for PAR) and dissolve to produce iodic acid (HIO_3) and elemental iodine (I_2).

Surely, metal iodides from various aerosols and/or IO_x are dissociated on the surface of the catalyst and can then produce gaseous I_2 by recombining the dissociated iodide, even without the existence of water.

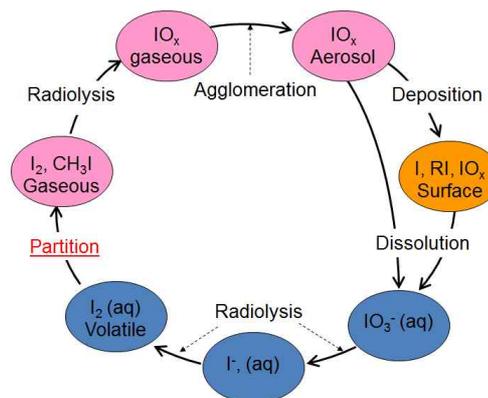


Fig. 1. Simplified iodine species cycle (copied from reference [2]).

2.2 Experimental set-up

Based on the iodine cycle in Figure 1, to study the effect of iodine, cesium iodide (CsI) and iodic acid (HIO_3) solids were applied into platinum on alumina (Pt/Al_2O_3 , 1 weight% loading) with the addition of few drops of water in a reaction flask, respectively. For the I_2 and CH_3I tests, they were vaporized to gases from I_2 at $60^\circ C$ and CH_3I at room temperature according to the method described in the published papers. Each of the produced I_2 (and CH_3I) and H_2 gases was mixed in a stainless steel ball mixer as the main gas flow before entering the reaction flask, including Pt/Al_2O_3 each. The conditions of air and 4.0% hydrogen were applied, and the flow of each gas was controlled by mass flow controllers (MFCs) for 30 minutes. The experimental set-up is shown in Figure 2.



Fig. 2. Photo of the iodine reaction test to Pt/Al_2O_3 .

3. Results and Discussion

Various iodines adsorbed on Pt/Al₂O₃ were studied by several physicochemical methods, including XRD, UV-vis, SEM-EDS, IR, XPS and Raman measurements. The XPS measured directly on the catalyst surfaces without scrapping. The binding energies (BEs) of iodine 3d reported by Smith and the XPS manual were 618.2 eV, 619.9 eV, 623.1 eV, 623.2 eV, 623.3 eV, 623.5 eV for CsI, I₂, HIO₃, HI₃O₈, I₂O₅, and NaIO₃, respectively. Based on the BEs of the samples, the iodines are in low BEs in the air condition compared to the H₂ present reducing condition as 617.68 eV, 623.19 eV, non-detectable, and non-detectable versus 619.14 eV, 623.86 eV, 618.22 eV, and 618.34 eV (shown partially in Figure 3). The BEs of I 3d for I₂ and CH₃I in contact with the Pt/Al₂O₃ catalysts were not detected in the air condition while they were detected under the H₂ condition. In addition, based on the shifts of the I 3d BEs, the oxidation state or shape may have changed under an oxidation or an H₂ conditions. The difference in BEs is known as 0.1 eV between the different oxidation states of the iodine oxides, and there is very little literature available about the BEs of different oxidation states for the iodine oxides. The very close BEs make it more difficult to analyze the XPS results further at the present state of things.

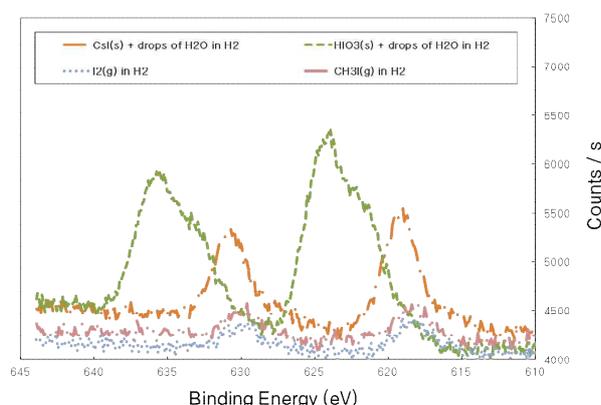


Fig. 3. XPS spectra of I 3d from some iodine species on Pt/Al₂O₃ under the H₂ Condition.

Acknowledgements

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