

A study of organic iodide removal mechanism using a silver ion exchanged zeolite

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1. Introduction

An organic iodide, especially, methyl iodide (CH_3I) would generated non-negligibly from a severe accident in a nuclear power plant. This CH_3I will be dangerous for human when it was inhaled, it is highly toxic and causes a serious nerve disorder. Even it is a major contributor to a thyroid cancer. In order to prevent its environmental release, it is required to decontaminate using a filtration system. There are two kinds of filtration methods, one is a wet-type using a pool scrubbing and the other is a dry-type using absorbents like zeolite, sand, charcoal, etc. For the removal of CH_3I from the release gases, wet-type is not ideal due to a high re-volatile characteristics of CH_3I . It may become volatile after dissolving in a pool and forms CH_3I again at the surface of water pool. Therefore, a dry-filtration should be installed to remove the CH_3I . In the previous study [1] by authors, we preliminary investigate the characteristics of zeolite filtration methods for the removal of CH_3I .

In this study, we investigate the removal mechanism of the organic iodide based on the previous study experimental data using the silver ion exchanged ZSM-5-zeolite (Ag^+ -ZSM-5). The chemical and physical adsorption characteristics of the silver ion exchanged zeolite are discussed in this paper.

2. Experimental details

The organic iodide adsorption tests were performed in the TGA-GC coupling system as shown in Fig 1.



Fig 1. TGA-GC coupling system

The TGA system measures the mass change of the sample in real time and the GC measures the content of CH_3I in off-gas in every 5 minute. As described in [1], the sample loading and the test procedure are in the following.

The zeolite (ZSM-5) sample was silver ion exchanged and it was confirmed that 7.2wt.% of silver ion was exchanged in the zeolite pores by the elemental analysis. In addition, the power-XRD was performed for the NH_4^+ form of ZSM-5 (before the silver ion exchange) and the Ag^+ -ZSM-5 as shown in Fig 2.

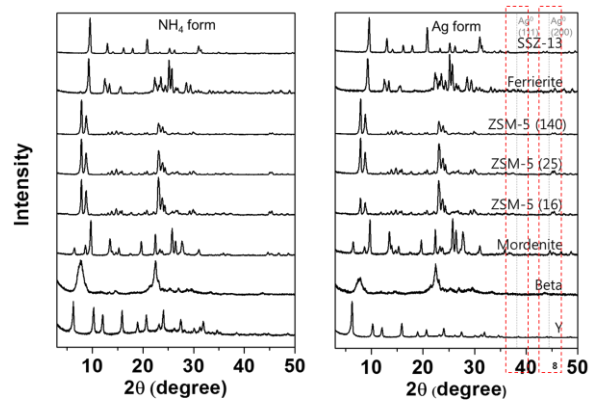


Fig 2. PXRD of zeolite powder (NH_4^+ form (left) and Ag^+ form(right))

As shown in Fig 2, no silver metal (Ag^0) peaks were found in both NH_4^+ and Ag^+ form, and it was confirmed that all the silver was contained in the zeolite pores in the ionic state.

The 20 mg of Ag^+ -ZSM-5 sample was loaded in the furnace of TGA as shown in Fig 3.

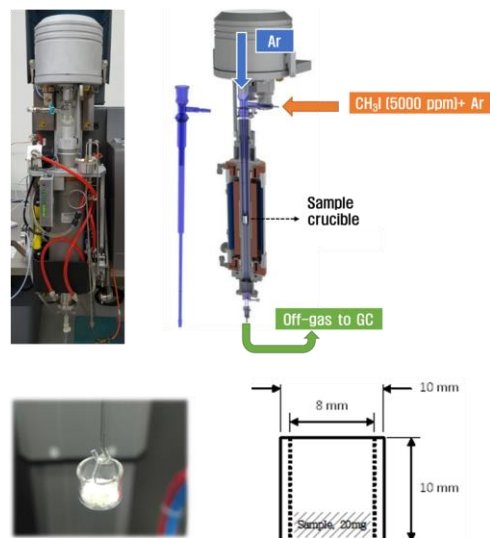


Fig 3. Sample loading in the TGA system

The test procedure is given in Fig 4.

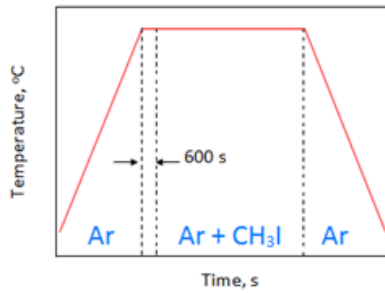


Fig 4. Test procedure

As shown in Fig 4, the target temperature was firstly achieved during the heating phase and the additional 600 second was required for the thermal stabilization. After the thermal stabilization phase, the isothermal phase was followed and the mass change was recorded in real time in this isothermal phase. The tests were performed at 50, 70, 90, 120, 150°C for 200 min.

3. Experimental results

The sample mass change measured by the TGA system at each temperature is provided in Fig 5.

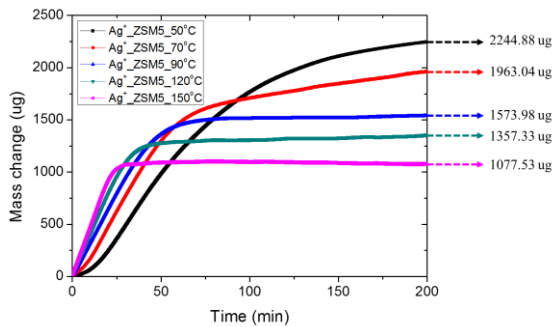


Fig 5. Mass change of samples

As shown in Fig 5, the initial adsorption rate is higher for the higher temperature, but the higher temperature sample was saturated earlier than the lower temperature. For this reason, the final mass gain of the sample is the highest at the lowest temperature sample. Around 1000-2200 µg of iodine was captured in the silver ion exchanged zeolite samples.

The mass balance analysis is performed for the reaction of the chemical adsorption of iodine by forming a silver iodide as follows:



The 20 mg of Ag⁺-ZSM-5 was used in each test and the 7.2wt% of silver ion is exchanged in the total mass of sample. Therefore, 1440 µg of silver ion is loaded in the

initial sample. If all of silver ion reacts with iodide and forms the silver iodide, 1694.13 µg of iodide should be captured by forming the silver iodide. Table 1 summarizes the mass balance analysis.

Table 1. Mass balance analysis

Reaction Stoichiometry			Limiting reagent	
Compound	Coefficient	Molar mass	Moles	Mass
Ag	1	107.87	13.35 * 10 ⁻⁶	1440.00 ug
I	1	126.90	13.35 * 10 ⁻⁶	1694.13 ug
AgI	1	234.77	13.35 * 10 ⁻⁶	3134.13 ug

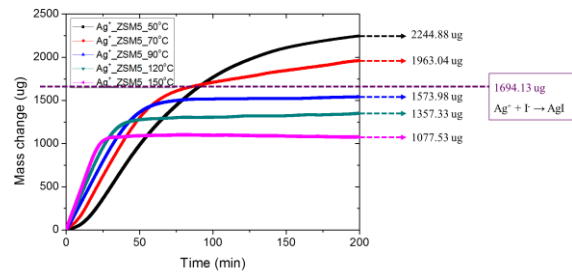


Fig 6. Mass change of samples with mass balance analysis

As shown in Fig 6, the samples of 50 and 70°C achieved higher mass gain than the calculated mass gain from the mass balance analysis. It seems that these additional mass gain might be from the physical adsorption by the zeolite porous structures. In contrast to the samples at 50 and 70°C, the samples of 90, 120, 150 °C showed less mass gain than the calculated mass gain. It also seems that these deficient amounts of mass would be the physical desorption due to the relative high temperature. These suspected physical adsorption and desorption amount was fitted with the Arrhenius equation which is generally used in the thermally-induced reaction.

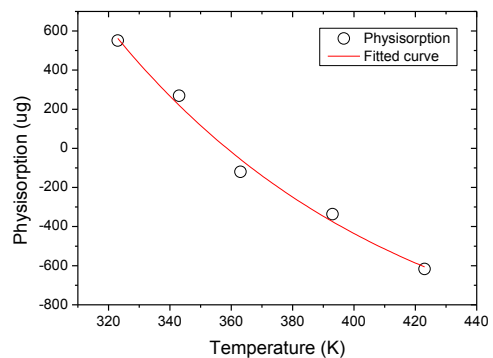


Fig 7. Physisorption amount

However, these physisorption mechanism is not fully understood at this moment, and further analysis should be required.

For the chemical adsorption between the silver ion and iodide, it is also thermally-induced reaction which would follow the Arrhenius equation. Therefore the initial reaction rate before the saturation point was fitted in the parabolic reaction rate law, and the activation energy was calculated as shown in Fig 8.

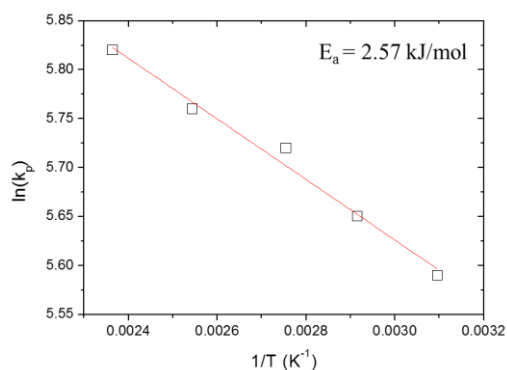


Fig 8. Reaction rate of chemisorption

As shown in Fig 8, at high temperature the reaction rate is high. In addition, the activation energy is calculated, that is the energy needs for the iodide to jump the barrier to be captured in the silver iodide in the zeolite pore. This chemisorption analysis needs further consideration for the detailed mechanism to understand better than current analysis.

3. Conclusions

In this study, the organic iodide capture mechanism in the zeolite porous structure is preliminarily discussed based on the tests data which is performed in the TGA-GC coupling system. Further analysis is ongoing to understand better the adsorption mechanism between the silver ion exchanged zeolite and the organic iodide.

ACKNOWLEDGEMENT

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REFERENCES

[1] Sanggil Park, Joonyoung Sung, Gi-ppeum Kim, Jaeyoung Lee, Organic iodide capture using a zeolite dry filtration, Transaction of the Korean Nuclear Society Spring Meeting, Jeju, Korea, May 18-19, 2017.