Ammonia Adsorption Properties of Natural Soil Adsorbent for Biohydrogen Purification

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In this study, we focused on the purification of biohydrogen by indirect pyrolysis. Syngas typically contains small amounts of impurities (e.g., NH₃), which negatively affect the fuel cell operation. Earlier, our group has developed removal technologies using solid adsorbents. Additionally, we estimated the adsorption performance considering environmental aspects based on life cycle assessment. In this study, we focused on the NH₃ removal capacities of two different adsorbents: hydroxyl aluminum silicate clay (HAS-Clay) and natural clay (Kanuma-Clay). We fabricated an experimental apparatus to evaluate the adsorption performance. The results show that the maximum adsorption of HAS-Clay is 2.90 g NH₃/100 g sorbent, whereas a maximum adsorption of 2.02 g NH₃/100 g sorbent was obtained by using Kanuma-Clay. Both adsorbents have the same allophane composition, which contributes to the adsorption performance. However, the environmental impacts of HAS-Clay and Kanuma-Clay differ. Thus, we evaluated their eco-burdens on the NH₃ removal.

Key Words
HAS-Clay, Kanuma Clay, LCIA, Bio-hydrogen, Adsorb NH₃

1. Introduction

Recently, hydrogen energy has been attracting attention as an alternative energy source that can be used to control global warming. Hydrogen can be produced from biomass feedstock which has a low environmental impact. Among different types of biomass, sewage sludge discharged at home is one of promising fuel resources. This can generate biogas at home through a fermentation system. In addition, hydrogen would be synthesized due to a reforming process. In the future, the demand for hydrogen in the households will increase with the increasing number of applications based on hydrogen (e.g. fuel cell-assisted bicycles, scooters, etc.). However, at present, hydrogen supplied to general consumers is mainly used for cars, and hydrogen stations are the main fueling facilities. Therefore, the hydrogen supply for mobile applications would still not be promoted in our residential sector. However, fuel cell scooters equipped with metal alloy storage tanks have
been developed in Taiwan and other countries, which also might have potential in our residential sector \textsuperscript{5}. Hydrogen is presumably stored in a H\textsubscript{2} tank at less than 1 MPa instead of a 35 MPa high-pressure tank. This means that the metal alloy storage tank can be operated more safely in comparison to the pressurized tank even though the fuel economy might be affected by the weight gain.

In a previous study, we designed the hydrogen purification system through a sewage sludge fermentation process. This system consists of fermentation, steam reforming, impurities removal, purification of pressure swing adsorption (PSA) and fueling processes \textsuperscript{2}. In general, biogas generated from sewage sludge contains approximately 3000 ppmv H\textsubscript{2}S and impurities such as NH\textsubscript{3} and HCl \textsuperscript{3}. These impurities adversely affect the catalysts used for the refinement of H\textsubscript{2} fuel and fuel cell operation. Therefore, these impurities must be removed. In addition, biogas contains approximately 40\% CO\textsubscript{2} \textsuperscript{4}, which reduces the reforming efficiency and leads to the consumption of a high quantity of fossil energy (e.g., electricity) during the purification of H\textsubscript{2}. Therefore, it is desirable to separate and remove CO\textsubscript{2} before the reforming process and/or use PSA as purification process to improve H\textsubscript{2} production efficiency. The adsorption system that was used for the removal of impurities can eliminate CO\textsubscript{2}, H\textsubscript{2}S, and NH\textsubscript{3} using hydroxyl aluminum silicate clay (HAS-Clay). HAS-Clay consists of hydroxyl aluminum silicates and low-crystalline clay and has been developed as an adsorbent for desiccant air conditioning systems \textsuperscript{6}. Previous tests showed that HAS-Clay can be recycled to remove CO\textsubscript{2} and H\textsubscript{2}S \textsuperscript{7}. Therefore, that is a physical adsorbent and has a good potential to repeatedly remove impurities at low temperature and low pressure. Although much energy is required for the production of HAS-Clay, it would cause low environmental impacts in a purification process in comparison to the conventional chemical adsorbent \textsuperscript{8}. On the other hand, it has been shown that CO\textsubscript{2} and H\textsubscript{2}S can be repeatedly adsorbed, but, the recyclability of NH\textsubscript{3} has not been investigated. Therefore, the adsorption performance of NH\textsubscript{3} was evaluated in this study. Through our adsorption test, the recyclability of NH\textsubscript{3} was not obtained. That is, HAS-Clay has less potential to eliminate NH\textsubscript{3} repeatedly. Due to this result, a different adsorbent with less environmental impact is needed. Therefore, we focused on Kanuma-Clay. Kanuma-Clay has also been applied to successfully remove HCl using PSA \textsuperscript{7}. It is named after the Kanuma-Clay mining region in the Tochigi Prefecture, Japan. It is pumice that formed from weathered volcanic ash and is usually used in Bonsai, cosmetics, and water purification systems due to its high moisture content \textsuperscript{8}. Kanuma-Clay has a pH of 5.25 and is an acidic soil \textsuperscript{9}. It has also been applied in the chemical industry sector to remove phosphorus from aqueous solutions \textsuperscript{10}.

### 2. Experimental

The removal experiment of NH\textsubscript{3} was executed using the following apparatus (see Fig. 1). For the NH\textsubscript{3} removal experiment, HAS-Clay (Toda Kogyo Corp.) and Kanuma-Clay (OBARI CO.LTD) were chosen (see Table 1). HAS-Clay possesses the functions of physical adsorption and sequestration of CO\textsubscript{2}. Regarding Kanuma-Clay, the same function would be expected. In a conventional NH\textsubscript{3} removal system, for instance, scrubbers such as water and polyethylene glycol have been used in removing NH\textsubscript{3} where the gas stream is passed through the scrubbing agent. Because NH\textsubscript{3} is soluble in water, that removal in aqueous chemical scrubbers becomes effective up to 99\%. However, it is said that a large amount of scrubber is needed making it expensive for small scale application \textsuperscript{11}. In addition, the indirect impacts of agent and the direct impacts of auxiliary power per would be extremely affected. Therefore, we investigated the possibility of recyclable adsorption of HAS-clay and/or the adsorption performance of low environmental impact material of Kanuma-Clay. In this experiment, a flow adsorption tube, that is, a stainless steel tube with an outer diameter of 12.7 mm and inner diameter of 10.7 mm, was used as our test apparatus. The experimental procedures on the adsorption test of HAS-Clay were as follows: (1) the adsorption tube was purged with N\textsubscript{2} at 50 mL/min to remove all oxygen, and (2) the inner tube was then heated to 40°C using a ribbon heater. The reason why the adsorption temperature is 40°C has an advantageous performance in lower temperature of HAS-Clay. Note that the space velocity (SV) was 1113.2 h\textsuperscript{-1}. Subsequently, (3) 400 mL of pure water was added to the beaker and (4) pH of pure water in the beaker was adjusted to 4.42–4.46 using a standard buffer (phthalic acid, pH: 4.0l) and aqueous sodium hydroxide (0.1 mol/L). Here, the dynamic pHs were measured using a portable pH/ORP meter (D-72, HIORIBA, Ltd.). After raising the designed temperature, a mixed sample gas of NH\textsubscript{3} and Ar (NH\textsubscript{3}: 100 ppm, Ar: balance) was flowed into the tube. The gas discharged from the tube was circulated in a beaker containing 400 mL pure water. Because NH\textsubscript{3} is water-soluble, a stirrer was used to make homogenize the solution. At the same time, the pH change of the solution was dynamically measured in use of a pH meter and the adsorbent breakthrough time was determined over the detection limit. That is, the point at which the pH rapidly increased is as the breakthrough point. Note that the initial pH changes at the time when 10020 ppmv NH\textsubscript{3} was flowed.
into the beaker. After the breakthrough point was reached, much amount of \( \text{N}_2 \) was flowed to rinse in the tube.

Next, we described the experiment of Kanuma-Clay. The experimental procedures are the same as those of HAS-Clay except the temperature changes of 50, 100, 150, and 213 °C, respectively. The last temperature condition is due to the temperature limit of a ribbon heater. The reason why the adsorption temperature was changed seems to be chemisorption in this case. That is, that would easily occur since the properties of Kanuma-Clay and \( \text{NH}_3 \) are acidic and alkaline. If the chemisorption would be caused, an increase in the temperature can favor the reaction between the adsorbate and the sorbent, thus enhancing the adsorption capacity. In this experiment, SVs at each temperature were 1167, 1385, 1416 and 1396 h\(^{-1}\), respectively. Note that the flow rate was set to 30 mL/min. Because the particle size of the Kanuma-Clay is relatively large (4.00-4.75 mm) and the sample gas would pass through the tube without any adsorption.

Regarding \( \text{NH}_3 \) adsorption in use of an acidic sorbent, chemisorption would occur. It means that the regeneration of adsorbent would be inhibited by this phenomenon. Therefore, we then investigated any structural changes of these adsorbents before and after the adsorption and desorption experiments. Here, the samples of HAS-Clay and Kanuma-Clay were observed by the scanning electron microscopy (SEM-EDS, JSM7001F, JEOL Ltd.). In addition, the Brunauer–Emmett–Teller (BET) surface areas were evaluated using the surface area and pore size distribution analyzer (BELSORP, MAX, MicrotracBEL Corp.).

Finally, based on the adsorption performance results, the environmental impacts of HAS-Clay and Kanuma-Clay were evaluated. Note that the environmental impacts on

| Specimen       | HAS-Clay | Kanuka-Clay |
|----------------|----------|-------------|
| Specific surface area [m\(^2\)/g] | 288      | 214         |
| Pore size [nm]  | 3.0      | 9.2         |
| Bulk density [kg/m\(^3\)]  | 1100     | 783         |
| Particle diameter [mm] | 0.15-1.00 | 4.00-4.75  |

Table 1 Characteristics of HAS-Clay\(^{13}\) and Kanuma-Clay

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basis of LCA methodology are the global warming potential (GWP) and abiotic depletion potential (ADP) which are due to database of CML. The estimation of these impacts was used by SimaProV8.2.0. The inventory data of HAS-Clay and Kanuma-Clay were based on our previous results. In this study, the functional unit is the amount of removed NH$_3$ per 100 g-sorbent [g-NH$_3$/100g-sorbent]. Note that the consumption amount of adsorbent to eliminate NH$_3$ per one cycle is estimated as the system boundary. In the case of Kanuma-Clay, the thermal energy is assumed to be provided by the exhaust heat from the steam reforming, if it is necessary to raise the adsorption temperature.

3. Results and Discussion

In this paper, we investigated the adsorption performance of NH$_3$ which is one of impurities contained in a biogas due to the basic experiments, and the environmental impacts were evaluated on basis of these performances. Especially, the regeneration of adsorbent would be extremely important in terms of the abatement of environmental impacts. Fig. 2 shows the relationship between the adsorption amount of HAS-Clay versus the number of adsorption test.

The results show that the adsorption amount increases when the HAS-Clay is activated; however, the adsorption gradually decreases thereafter. According to this result, the regeneration of HAS-Clay seems to be inhibited. That is, it implies that HAS-Clay for NH$_3$ adsorption is not repeatedly used. The difference between 3rd and 8th adsorption test was 1.89 g NH$_3$/100 g adsorbent, which was approximately 63.0% decrease. It is understood that HAS-Clay would chemisorb NH$_3$. Here, we observed the configuration change of HAS-Clay before and after adsorption test (see Fig. 3). Note that the SEM image after the test was taken by the sample subsequent to the 8th cycle. Fig. 3 show the SEM images of the HAS-Clay (100 nm scale). However, any configuration change is not observed. The performance drop is not likely to be a configuration issue. The detail investigation of the performance drop due to the configuration change will be the subject of future research.

In addition, the surface areas before and after the tests were evaluated (see Fig. 4). From this result,
we recognized that the surface area decreased by approximately 15%. It was suggested that the chemisorption of HAS-Clay occurred in this test. It is known that chemisorption changes the surface condition\(^\text{14}\). That is, due to the reaction of NH\(_3\) with HAS-Clay, we imagine that the pores are filled and that the surface area is reduced. Thus, we guessed that HAS-Clay cannot be repeatedly used.

Next, Fig. 5 shows the results of repeated adsorption experiments using Kanuma-Clay at 50°C. According to Fig. 5, the adsorption amount decreases by repeating the cycle from the early stage. This obviously indicates that NH\(_3\) is chemisorbed by Kanuma-Clay. Because the sorbent property is acidic.

Likewise, we observed any changes before and after the test on basis of SEM image and BET surface area (see Figs. 6 and 7). Note that the SEM image after the test was taken by the sample subsequent to the 4th cycle. In Fig. 6, the pores of clay seem to be filled in spite of the less cycles of HAS-Clay case. However, because Kanuma-Clay is a natural soil and inhomogeneous, it remains uncertain whether the pores are really filled by NH\(_3\) adsorption. On the other hand, there was obvious difference on the result of BET surface area (see Fig. 7). We estimated approximately 11% reduction of the surface area before and after the test. Based on the above results, this indicates that Kanuma-Clay acts as the sorbent of chemisorption.

According to URSU et al. they said that a solid acid clay namely acid-activated montmorillonite, the major fraction of the bentonitic natural clay, was utilized as adsorbent for ammonia. Through their experiments, they indicated that the performance dropped due to the repeatedly used clay sorbent\(^\text{15}\). Therefore, we understood that the same phenomena occurred in Kanuma-Clay. In addition, the temperature effect was discussed in Kanuma-Clay. Because some species, which would be acted as catalysts, are contained in the natural soil. If the adsorbent temperature is rising, the reaction between the adsorbate and the sorbent would be more suitable. That is, the capture capacity was expected to increase. Thus, we measured the capture capacity of NH\(_3\) varying the temperature (see Fig. 8). Unfortunately, On the temperature effect, the benefit would not be obtained even if the adsorption temperature increases. Furthermore, the extra thermal energy which
can be compensated with the exhaust energy is not necessary.

The maximum adsorptions of both clays were 2.90 g-NH3/100 g-adsorbent of HAS-Clay and 2.02 g-NH3/100 g-adsorbent of Kanuma-Clay, respectively. This means that the two sorbents are not suitable to repeatedly use.

Finally, we show the result of impact analysis. From our experimental results, we consider the alternation of HAS-Clay with Kanuma-Clay. In terms of eco-burden mitigation, Kanuma-Clay has a good potential to be used as an alternative adsorbent for HAS-Clay, since the specific eco-burden of Kanuma-Clay would be lower in comparison to that of HAS-Clay (see Table 2). Here, using the maximum adsorption amount of each adsorbent, the GWP and ADP were evaluated (see Fig. 9). Note that the units of GWP and ADP are kg-CO2 eq./g-NH3 and kg-Fe eq./g-NH3. As a result, the eco-burdens of Kanuma-Clay were obviously improved in comparison to those of HAS-Clay. For instance, The HAS-Clay is artificially produced, and a lot of energy should be required in its production process. While, the much eco-burden is not impacted in terms of LCA concept, since Kanuma-Clay is a natural clay. Considering the dry removal system of NH3, Kanuma-Clay would be a promising candidate as a sorbent.

Table 2 Specific eco-burdens of HAS-Clay and Kanuma-Clay

| Specimen      | HAS-Clay | Kanuma-Clay |
|---------------|----------|-------------|
| Impact        |          |             |
| Climate change (GWP) [kg-CO2 eq./100g-sorbent] | 1.71 | 4.00 x 10^{-4} |
| Material depletion (ADP) [kg-Fe eq./100g-sorbent] | 1.50 x 10^{-2} | 1.00 x 10^{-4} |

Fig. 9 Results of the impact categories of GWP and ADP

4. Conclusion

This study discussed the eco-burden of the removal procedures using HAS-Clay or Kanuma-Clay on basis of the experimental results. Through the adsorption tests, we demonstrated that the adsorption of NH3 due to HAS-Clay or Kanuma-Clay was chemisorption. Therefore, these clays cannot be used repeatedly for the adsorption of NH3. In this study, the eco-burdens were analyzed based on experimental results using an LCA approach based on GWP and ADP indicators. We found that both HAS-Clay and Kanuma-Clay can eliminate NH3 in biogas for Bio-H2 fuel. However, the eco-burdens of Kanuma-Clay is more beneficial. Consequently, the GWP of HAS-Clay and Kanuma-Clay were 5.92 x 10^{-1} and 1.99 x 10^{-4} kg-CO2 eq./g-NH3, respectively. Furthermore, the ADP of HAS-Clay and Kanuma-Clay were 5.18 x 10^{-3} and 4.96 x 10^{-5} kg-Fe eq./g-NH3, respectively. Hence, we conclude that Kanuma-Clay should be used as an alternative NH3 adsorbent in terms of eco-design concept. In the future, for the detail process...
design, we have a plan to carry out the project including the verification demo-test. Through this demo-test, we will estimate the eco-indicators of GWP and/or ADP considering the operating data.

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