

Trace Ammonia Equilibrium Pressure of Zirconium Phosphate in Moisture

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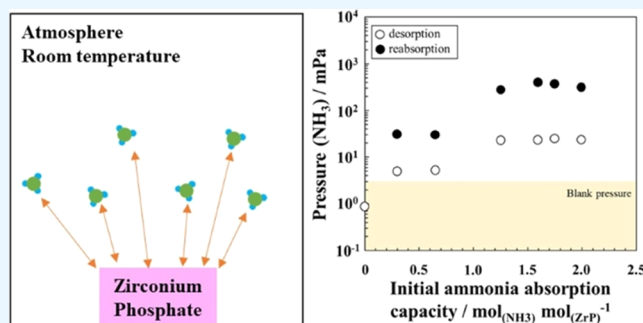
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ABSTRACT: Zirconium phosphate-absorbed ammonia gas and the ammonia concentration (pressure) decreased to 2 ppm (ca. 20 Pa). However, it has not been clarified what the equilibrium pressure of zirconium phosphate is during ammonia gas ab/desorption. In this study, the equilibrium pressure of zirconium phosphate during ammonia ab/desorption was measured using cavity ring-down spectroscopy (CRDS). For ammonia-absorbed zirconium phosphate, a two-step equilibrium plateau pressure was observed during the ammonia desorption in gas. The value of the higher equilibrium plateau pressure at the desorption process was about 25 mPa at room temperature. If the standard entropy change (ΔS^0) of the desorption process is assumed to be equal to the standard molar entropy of ammonia gas (192.77 J/mol_{(NH₃)/K), the standard enthalpy change (ΔH^0) is about -95 kJ/mol_{(NH₃). In addition, we observed hysteresis in zirconium phosphate at different equilibrium pressures during ammonia desorption and absorption. Finally, the CRDS system allows the ammonia equilibrium pressure of a material in the presence of water vapor equilibrium pressure, which cannot be measured by the Sievert-type method.}}



INTRODUCTION

Alternative fuels to replace fossil fuels continue to be actively developed toward a carbon-free society. One of the alternative fuels is ammonia.^{1–3} Ammonia is attracting attention as a carbon-free (green ammonia) and carbon-neutral (blue ammonia) fuel.^{3,4} Demand for ammonia is expected to continue to increase in the future. On the other hand, ammonia is a toxic chemical to humans. For example, the American Conference of Governmental Industrial Hygienists (ACGIH) has set the allowable concentration of ammonia at 25 ppm as the exposure limit at workplace (threshold limit value-time weighted average; TLV-TWA).⁵ In addition, the concentration at which humans perceive ammonia as a bad odor is considered to be around a few ppm.^{6,7} Therefore, in order to handle ammonia safely, ammonia removal methods are required to quickly remove ammonia to below the concentration mentioned above, such as at the time of a leakage. In addition, for daily use, it is necessary to have a method to quickly remove ammonia gas to an ammonia concentration below that recognized as a bad odor.

Currently, the response to ammonia leakage is to spray water at the leak site.^{8,9} However, for example, to reduce the ammonia gas concentration to 25 ppm or less at room temperature, the ammonia concentration in the water has to be reduced to 25 ppm or less due to vapor pressure.^{10,11} In the case of ammonia leakage, it is estimated that at least several

grams of ammonia leak out, and in the case of a building, the ammonia concentrations are estimated to be over 1,000 ppm. Thus, to remove ammonia to an allowable concentration, more than 10,000 times the weight of water is needed relative to the leak weight of ammonia. Furthermore, before ammonia-containing water is released into the environment, it must be treated in some way to prevent eutrophication.¹² Accordingly, a new material that can easily and quickly remove ammonia to a safe concentration is considered necessary.

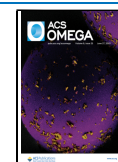
In a previous study, we proposed zirconium phosphate ($\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, ZrP) as an ammonia removal material.¹³ Zirconium phosphate decreased the ammonia concentration (pressure) in the atmosphere from 1000 to 2 ppm (ca. 0.2 Pa).¹⁴ However, it has not been clarified what the equilibrium concentration (pressure) of zirconium phosphate is during ammonia gas sorption.

In general, when a material sorbs gas, the ambient equilibrium pressure changes depending on the amount of gas sorbed by the material.^{15–18} Thus, pressure composition

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isotherms or adsorption isotherms are measured with the amount of gas sorption in the material and the equilibrium pressure around the material. When measuring the ammonia equilibrium pressure of a material, the Sievert-type apparatus is currently used to measure pressure composition isotherms. However, since the measurement limit is about 10 Pa (1 ppm),¹⁹ ammonia equilibrium pressure of zirconium phosphate is difficult to determine by the current equipment. In addition, zirconium phosphate has water of crystallization and has water vapor equilibrium pressure. Since the Sievert-type method measures total pressure to quantify sorption capacity and equilibrium pressure, a method to measure ammonia and water separately is necessary. Although it is possible to measure only the ammonia pressure using a Kitagawa-type detector, continuous measurement is difficult, and some ammonia gas is sorbed by the detector tube.^{19,20} Thus, we considered ammonia equilibrium pressure measurement requires a different method. The cavity ring-down spectroscopy (CRDS) is a continuous measurement method that can measure ammonia pressure and water vapor pressure, and it can measure trace ammonia pressure at the mPa level.^{19,21}

In this report, we have studied equilibrium states between zirconium phosphate and ammonia gas under the atmosphere. The ammonia ab/desorption characteristics of zirconium phosphate were investigated using ammonia pressure composition isotherm with CRDS and powder X-ray diffraction (XRD).

EXPERIMENTS

Materials. We used zirconium phosphate ($\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, ZrP) with a layered structure (α -zirconium phosphate, CZP-100 manufactured by Daiichi Kigenso Kagaku Kogyo Co., Ltd.). ZrP was used as received without further purification.

We used ammonia water (10 wt %, manufactured by KENEI Pharmaceutical Co., Ltd.). Various ammonia concentrations of ammonia water were prepared by 10 wt % aqueous ammonia from KENEI Pharmaceutical Co., Ltd., diluting with ion exchange water. The ammonia concentration was estimated from the ammonia meter (Orion Star A324 and Orion 9512 manufactured by Thermo Scientific Orion; minimum detection limit: 0.01 ppm) and pH meter (CyberScan pH310 manufactured by EUTECH Ins.) measurements. In ammonia water, ammonia has two forms (NH_3 and NH_4^+). For ammonia absorption of zirconium phosphate, the NH_3 and NH_4^+ concentration in the solution should be evaluated. NH_3 concentration ($[\text{NH}_3]$) was measured by the ammonia meter. Then, NH_4^+ concentration ($[\text{NH}_4^+]$) was calculated using the following eq 1:

$$[\text{NH}_4^+] = \frac{K_b}{10^{\text{pH}-14}} [\text{NH}_3] \quad (1)$$

where K_b is the base dissociation constant ($K_b = 1.8 \times 10^{-5}$ M at 298 K) and pH is the potential of hydrogen.²²

Zirconium phosphate was put into ammonia water of various ammonia concentrations, respectively. The ammonia absorption capacity (C_{ab}) of zirconium phosphate was calculated by the following eq 2, as in previous studies:^{23,24}

$$C_{\text{ab}} = ([\text{NH}_3]_{\text{af}} + [\text{NH}_4^+]_{\text{af}} - [\text{NH}_3]_{\text{be}} + [\text{NH}_4^+]_{\text{be}}) \times L \quad (2)$$

where $[\text{NH}_3]_{\text{be}}$ and $[\text{NH}_3]_{\text{af}}$ are NH_3 concentrations before and after ZrP is added, $[\text{NH}_4^+]_{\text{be}}$ and $[\text{NH}_4^+]_{\text{af}}$ are NH_4^+

concentrations before and after ZrP is added, and L is the volume of ammonia water.

Then, zirconium phosphate with different ammonia absorption capacities was prepared by vacuum drying for at least half a day. At this time, it has been confirmed that the ammonia and crystalline water in the samples are hardly released, and the water on the surface of the samples is removed.^{23,24}

Ammonia Desorption and Reabsorption Measurements. A cavity ring-down spectroscopy laser system (G2103 gas concentration analyzer manufactured by Picarro, Inc.), a diaphragm pump, a mass flow controller, a heater, and a thermometer were used to circulate the gas in the measurement vessel, connected as shown in Figure 1. The volume of the entire measuring apparatus is about 50 mL.

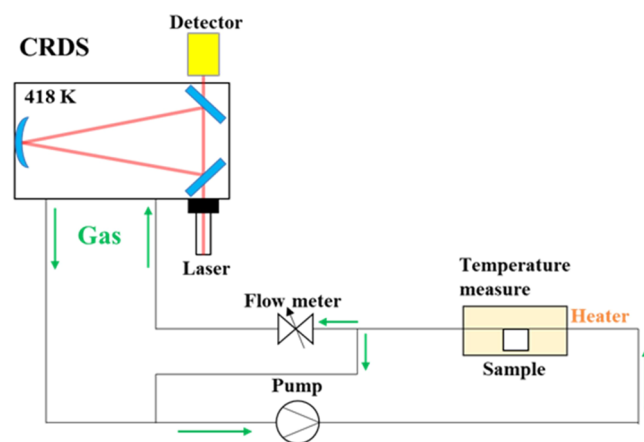


Figure 1. Schematic diagram of the ammonia pressure composition isotherm measurement by using CRDS.

The ammonia pressure of about 3 mPa was used as the measurement limit because the atmosphere used during the measurement originally contained ammonia at a maximum of about 30 ppb (3 mPa). In addition, the water vapor was 1000 ± 200 Pa.

The ammonia pressure composition isotherm of zirconium phosphate was measured using the apparatus shown in Figure 1. First, the equilibrium pressure of zirconium phosphate during ammonia desorption was measured. About 50 mg of zirconium phosphate, each with a different ammonia sorption capacity, was placed in the sample container. The ammonia pressure at which the 10 h error was within 10% was taken as the equilibrium pressure at the time of desorption.

Next, the equilibrium pressure of zirconium phosphate during ammonia absorption was measured. Since the operating range of the CRDS system is 10 ppm (ca. 1 Pa), it is necessary to mix ammonia gas so as not to exceed this concentration. However, it is difficult to prepare ammonia gas of this concentration and flow it into the system. Therefore, the sample was heated to desorb some ammonia. The heating temperature was controlled at 323–333 K to prevent condensation from occurring in the apparatus due to water vapor released from the sample. Then, by returning the sample to room temperature, the ammonia was adsorbed into the sample. The ammonia pressure at which the 10 h error in the ammonia pressure measured by the CRDS system fell within 10% was used as the equilibrium pressure at the time of absorption. The molar ratio between the maximum ammonia

desorption and zirconium phosphate at this time is theoretically less than 10^{-4} mol_{(NH₃)/mol_(ZrP) when calculated using the ideal gas equation of state, since the conditions are dilute at 1 Pa.}

From the results of the equilibrium pressure of zirconium phosphate at each ammonia desorption and reabsorption and the initial ammonia absorption of zirconium phosphate at that time, an ammonia pressure composition isotherm for zirconium phosphate was developed.

X-ray Diffraction Analysis. Powder X-ray diffraction measurements of zirconium phosphate after ammonia absorption and desorption were also performed to confirm the crystal structure change of zirconium phosphate due to ammonia absorption and desorption. XRD patterns were recorded on a Bragg–Brentano diffractometer (Rigaku RINT-2500V manufactured by Rigaku Co.) and Cu K α at a tube current of 200 mA and tube potential of 40 kV. Before XRD measurements, all samples were evacuated at room temperature for 20 h to remove water from the surface of zirconium phosphate after ammonia absorption and desorption. Each sample was pressed at a constant load on a glass holder.

RESULTS AND DISCUSSION

The equilibrium pressure during ammonia desorption and reabsorption of ammonia from ammonia-absorbing zirconium phosphate in air was measured using a CRDS system. Figure 2 shows the time variation of ammonia desorption pressure of ammonia-absorbing zirconium phosphate with different ammonia sorption capacities.

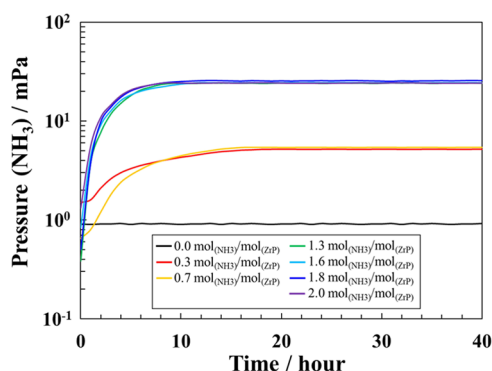


Figure 2. Relation between the NH₃ desorption pressure and time of samples at 292–296 K.

Zirconium phosphate with an initial ammonia sorption capacity of 0–1 mol_{(NH₃)/mol_(ZrP) desorbed about 5 mPa of ammonia in half a day. Zirconium phosphate with an initial ammonia sorption capacity of 1–2 mol_{(NH₃)/mol_(ZrP) desorbed about 25 mPa of ammonia in half a day. Since the ammonia pressure remained constant for more than 10 h after that, this pressure was used as the equilibrium pressure for the ammonia desorption of the zirconium phosphate with ammonia absorption.}}

Figure 3 shows the time variation of ammonia pressure when ammonia was absorbed in zirconium phosphate after ammonia desorption.

The initial ammonia pressure was shifted because the measurement was started after heating once and then air-cooling to room temperature. For zirconium phosphate with an initial ammonia absorption of 0–1 mol_{(NH₃)/mol_(ZrP), the}

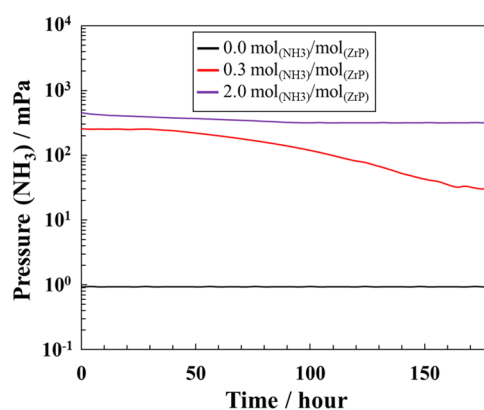


Figure 3. Relation between the NH₃ reabsorption pressure and time of samples at 290–300 K.

ammonia pressure decreased to about 250 mPa in half a day. This is similar to the ammonia pressure during ammonia removal for zirconium phosphate alone measured in previous studies. The ammonia pressure then decreased further, and after a week, the difference in ammonia pressure over a 10 h period was within 10%. At this time, the ammonia pressure was about 30 mPa. In the previous study,^{13,14} the measurement started at an initial ammonia pressure of 100,000 mPa and ended after about 4 h, suggesting that the equilibrium pressure had not been reached. For zirconium phosphate with an initial ammonia sorption capacity of 1–2 mol_{(NH₃)/mol_(ZrP), the ammonia pressure decreased gradually for several days starting at about several hundred mPa; when the difference in ammonia pressure over 10 h was within 10%, the ammonia pressure was about 300 mPa. Thus, the ammonia originally absorbed in each sample did not return to its original state, respectively, and the ammonia reabsorption pressure was higher than the ammonia desorption pressure. It is regarded as a kind of hysteresis. The possible reasons are that the absorption reaction of materials is not in equilibrium due to their slow ammonia absorption rate or that materials have different ammonia absorption and desorption processes.^{18,25,26}}

As the materials ab/desorb ammonia, the crystal lattice shows expansion and contraction as the ammonia content changes. In the absorption process, an activation barrier exists because some of the energy is consumed in the expansion of the lattice atoms. However, in the desorption process, the atoms contract freely without releasing energy.²⁷ Thus, it is suggested that the desorption pressure is the thermodynamic equilibrium pressure. Therefore, it is considered that the desorption pressure is the ammonia equilibrium pressure for zirconium phosphate.

XRD patterns were performed to measure the changes in the samples before and after ammonia desorption and reabsorption. Figure 4 shows XRD patterns of the sample that absorbed 2 mol_{(NH₃)/mol_(ZrP) ammonia after each experiment. The sample showed no change in their XRD patterns before and after ammonia desorption and reabsorption. The XRD patterns of each sample were also unchanged before and after the experiment. Therefore, it is suggested that the ammonia absorption capacity of each sample is the initial ammonia absorption capacity.}

From the above, Figure 5 shows the ammonia pressure composition isotherm (PCI) for zirconium phosphate with the horizontal axis as the initial ammonia absorption of zirconium

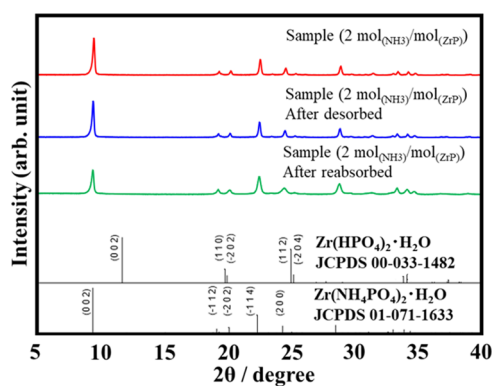


Figure 4. XRD patterns of 2 mol_(NH₃)/mol_(ZrP) ammonia-absorbed ZrP before desorption, after desorption at R.T., after reabsorption, Zr(HPO₄)₂·H₂O (JCPDS: 00-033-1482), and Zr(NH₄PO₄)₂·H₂O (JCPDS: 01-071-1633).

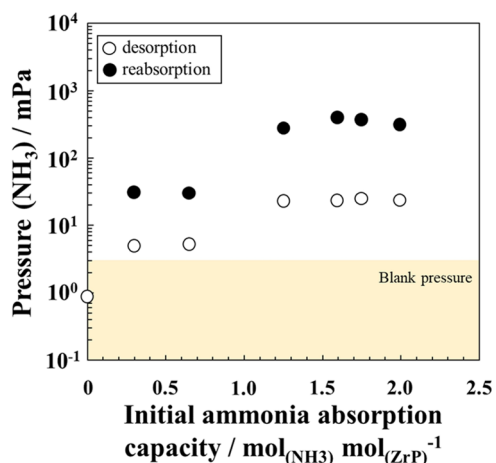
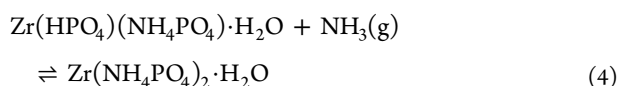
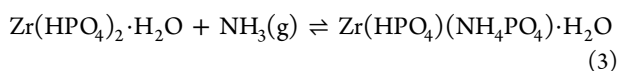


Figure 5. Ammonia pressure composition isotherm of zirconium phosphate-absorbed ammonia at 290–300 K.

phosphate and the vertical axis as the ammonia equilibrium pressure measured by the CRDS system. The ammonia pressure composition isotherms for zirconium phosphate, similar to the ammonia concentration composition isotherms for zirconium phosphate in ammonia water in our previous study,²³ suggest the possibility of a two-step equilibrium plateau region in the range of 0–1 and 1–2 mol_(NH₃)/mol_(ZrP). Thus, when zirconium phosphate absorbs ammonia, the noncovalent electron pair of ammonia is considered to be coordinated to the proton of zirconium phosphate. The following reactions are considered:



The standard enthalpy change (ΔH^0) and entropy change (ΔS^0) of the corresponding ammonia absorption equilibrium reaction of zirconium phosphate can be evaluated from the plateau pressure (P_{eq}) and experimental temperature (T) according to the following van't Hoff equation:

$$\ln\left(\frac{P_{\text{eq}}}{P^0}\right) = \frac{\Delta H^0}{RT} - \frac{\Delta S^0}{R} \quad (5)$$

where P^0 is the standard pressure.²² Since ammonia (gas) reacts with zirconium phosphate (solid) and is incorporated into the solid as ammonium ions, the absolute value of ΔS^0 is assumed to be equal to the standard molar entropy of ammonia gas (192.77 J/(mol_(NH₃)·K)²⁸). Therefore, ΔH^0 of reaction 3 and reaction 4 are −100 and −95 kJ/mol_(NH₃), respectively. ΔH^0 is the enthalpy difference between the enthalpy of the reactants and the enthalpy of the products and is uniquely determined, independent of the path. Therefore, the standard enthalpy change of reaction 4 (−95 kJ/mol_(NH₃)) is almost equal to the total of the standard enthalpy change obtained for the ammonia CCI (−64.1 kJ/mol_(NH₃))²⁴ and the standard enthalpy change of ammonia dissolved water by Henry's law data (−30 kJ/mol_(NH₃)).¹⁰ However, the standard enthalpy change of reaction 3 is not equal to the total of the standard enthalpy changes obtained by the ammonia CCI and Henry's law data. In order to determine the cause, it will be necessary to generate ammonia pressure composition temperature plots with various temperatures in order to calculate ΔH^0 and ΔS^0 .

The water vapor pressure of each sample was about 1500 Pa at room temperature. Therefore, zirconium phosphate has a water vapor equilibrium pressure of about 1500 Pa at room temperature. Since this water vapor equilibrium pressure is over 1000 times higher than the ammonia absorption and release pressure of the same material, it is considered difficult to measure the ammonia absorption and release properties by the Sievert-type method. Therefore, for materials such as zirconium phosphate, which has a low ammonia equilibrium pressure and crystal water, it is essential to use a CRDS system that can separate water and ammonia for measurement.

CONCLUSIONS

The equilibrium pressure of zirconium phosphate during ammonia absorption and release was measured by a CRDS laser system. From the relation between the measured equilibrium pressure and the ammonia absorption of zirconium phosphate, an ammonia pressure composition isotherm for zirconium phosphate was prepared. The results suggest that zirconium phosphate has a two-step ammonia equilibrium plateau pressure. This is similar to the ammonia concentration composition isotherms of zirconium phosphate observed in ammonia water. In addition, we observed hysteresis in zirconium phosphate at different equilibrium pressures during ammonia desorption and absorption.

The CRDS system allows the ammonia equilibrium pressure of a material in the presence of water vapor equilibrium pressure, which cannot be measured by the Sievert-type method.

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Notes

The authors declare no competing financial interest.

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