FULL PAPER

Ion exchange of layered titanate with transition metal and application to ammonia storage

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Layered titanates including transition metal in interlayer space were prepared by ion exchange process. Ammonia adsorption was performed into the transition metal-including layered titanates by aqueous liquid and gas phase. X-ray diffraction patterns of the sample with aqueous liquid and gas phase adsorption confirm that ammonia can be adsorbed without collapse of the titanate layered structure. Further, there was a large increase in the ammonia adsorption amount for the sample with gas phase adsorption comparing to that with the aqueous liquid phase adsorption. Such large amount of ammonia adsorption results from the elimination of the water molecules coordinated with the metal cation between the layers by preheating.

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1. Introduction

Currently, environment and energy issues are being debated from various viewpoints such as a consumption of fossil fuel, environmental pollution and global warming.^{1)–3)} From now on, new energies that can provide stable supply are required. There are some candidates for energy carrier materials, liquid-phase hydrogen, organic hydride, ammonia, metal magnesium, methanol and so on.^{4)–6)} Among them, ammonia is attracting attention as a reasonable energy carrier. Ammonia has a hydrogen content of approx. 18 mass % in the molecule containing no carbon, and the burden on the environment can be diminished. In addition, procurement costs can be very low because ammonia can be produced all over the world. Liquid ammonia is relatively easy to prepare and its density is approximately 0.6 to 0.7 g/cm³ which is 10 times larger than that of liquid hydrogen. These features become large advantages as a hydrogen storage medium.^{7),8)}

Ammonia is generally used for wide applications. For example, it is used as a base material for fertilizers, reducing agent, external medicine, coolant etc.^{9),10)} In recent years, a fuel cell using ammonia as a fuel has been developed.¹¹⁾ Opportunities for use of ammonia will tend to

increase in the future. Ammonia can be stored as an aqueous liquid or gas state. However, the solution is necessary to separate into ammonia and water, and the gas has a risk of leakage. Safe storage is necessary for ammonia because it has a stimulative odor, toxic substance, lethal dose (30 mL in 25% aqueous solution). Therefore, storage of ammonia molecule and reasonable process for ammonia treatment are required.

Lepidocrocite-type layered titanate is a compound having a layered structure. The layers composed of edge shared TiO₆ octahedra and alkali metal ions such as Na, K, Rb and Cs are intercalated for charge compensation. A part of the titanium site is vacancy for Cs-type, and is substituted with other mono-, di- or trivalent metal ions for Na, K and Rb-types in the interlayer.^{12),13)} An interlayer cation is generally possible to exchange by a protons and then by other metal cations. The matrix phase has the similar properties as titanium oxide, solid acidity and photocatalytic activity.¹⁴⁾

In this paper, we synthesized a lepidocrocite-type layered titanate using Cs in interlayer space for use as a storage material for ammonia because there are no substitutes in the intralayer position. Various metal cations were introduced between the layers to evaluate the ammonia adsorption characteristics. It is well known fact that some metal cations can form ammine complexes. Therefore, competency and an actual mechanism for adsorption and desorption of ammonia were examined for an application of ammonia storage materials.

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2. Experimental procedure

2.1 Synthesis

The lepidocrocite-type layered cesium titanate was synthesized by a conventional solid-state process as follows. Cs_2CO_3 and TiO_2 were mixed wetly and the intimate mixture was placed in an alumina crucible. Then, it was heated at 800°C for 1 h for decarbonation. The mixture was then heated two times at 800°C for 20 h in air. The sample was ground with each cycle. The resultant sample was designated as CTO.

The as-prepared layered titanate was protonated by ion-exchange in HCl aqueous solution as follows. CTO was stirred in HCl solution (solution/solid = 200 mL/g) at room temperature for 1 week. The HCl solution with 0.2, 0.5, 0.8 and 1.0 mol/L concentration was used in this process. The solution was replaced by a fresh one everyday to promote the protonation. After that, the protonated sample was separated by centrifugation at 12000 rpm for 5 min, washing several times and drying at 50°C . The resultant sample was named as HTO.

Layered titanate with intercalation of metal cation was formed by ion exchange. Some sorts of solution were prepared by adding metal acetate or nitrate (Ca, Mn, Co, Ni, Cu and Ag) twice of molar ratio as much as the amount of HTO to ultrapure water of 25 mL. HTO was then added to this solution (solution/solid = 250 mL/g) and stirred at 40°C for 3 days. After filtration, the samples were washed and dried at 50°C . These samples were designated as M-HTO (M: Ca, Mn, Co, Ni, Cu or Ag).

2.2 Ammonia adsorption and desorption

The layered titanates with metal cation were examined for adsorption of ammonia via an aqueous liquid and a gas phase. In the case of aqueous liquid adsorption, samples were soaked in ammonia aqueous solution (30% concentration) for 3 days. After soaking, the sample was filtered and dried at room temperature. The obtained samples were designated as M-HTO- NH_3aq . In the case of gas adsorption, samples were heated at 150°C for pretreatment by which adsorbed H_2O molecules on the interlayer cation can be removed. Then, the pretreated samples were kept in pure ammonia gas (1.0 L/g) for 16 h. The obtained samples were designated as M-HTO- NH_3gas .

Ammonia desorption was characterized by heat treatment. For the heat treatment, the M-HTO- NH_3aq sample was analyzed by TG-DTA and TG-MASS. For the TG-MASS measurement, we paid attention to m/z values of 16, 17 and 18 for determination of ammonia desorption temperature. **Table 1** shows ammonia and water fragmentation patterns. From the table, ammonia and water can be distinguished by the signal of 16 and 18 of m/z .¹⁵⁾

Table 1. Ammonia and water fragmentation patterns

m/z	14	15	16	17	18	19	20
NH_3	2.2	7.5	80.1	100.0	0.4	—	—
H_2O	—	—	0.9	21.2	100.0	0.5	0.3

2.3 Characterization

Powder X-ray diffraction (XRD) patterns were measured at ambient temperature by $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) with accelerating voltage of 40 kV and tube current of 15 mA with a scanning rate of 10° at $2\theta \text{ min}^{-1}$ (MiniFlex600 Rigaku). FT-IR spectra were recorded by Fourier transform infrared spectrometer (FT/IR-4100, JASCO CORPORATION) using KBr method. All samples were measured in transmission mode with the wave number of $400\text{--}4000 \text{ cm}^{-1}$. The particle shape and chemical composition were observed by FE-SEM (JSM-6500F, Hitachi). The Amount of ammonia was measured using CHN Coder (MT-5, Yanaco). In the measurements, p-nitroaniline was used as standard sample. The TG-MASS measurements were taken at the range from room temperature to 1000°C with the rate of $10^\circ\text{C min}^{-1}$ in flowing He (Thermo-MASS, Rigaku).

3. Results and discussion

3.1 Preparation of cation exchanged layered titanate

Figure 1 shows XRD patterns of CTO and HTO treated by various concentrations of HCl as a protonation agent. The diffraction peak (020) at around 10° in 2θ , which indicates interlayer spacing, is quite small in CTO because intercalated Cs cation has relatively large atomic mass. The chemical formula of CTO was determined to $\text{Cs}_{0.70}\text{Ti}_{1.825}\text{O}_4$. By protonation, intensity of the peak increases steeply due to drastic decrease of electronic density between layers for the sample by 0.2 and 0.5 M HCl. This phenomenon can be regarded as a collateral evidence for replacement of Cs cation by proton. However, the diffraction peaks become broad on further higher concentrations of HCl. These patterns confirm anatase emergence. Actually, the protonation degree of each samples are 75, 97, 98 and 91% for 0.2, 0.5, 0.8 and 1.0 M, respectively. Therefore, optimal concentration of HCl seems to be 0.5 M.

Fig. 1. XRD patterns of CTO and HTO protonated by various concentration of HCl.

Fig. 2. XRD patterns of ion exchanged samples using metal nitrates.

Fig. 3. XRD patterns of ion exchanged samples using metal acetates.

Figure 2 shows the XRD patterns of the ion exchanged samples using metal nitrates. Except for Ag-HTO, these samples show diffraction peaks (020) at around 10° indicating interlayer spacing of the lepidocrocite-type structure. Consequently, metal cations could be introduced between the layers while maintaining the layered structure. However, the diffraction peaks seem to broaden and the crystallinity declines. For Ag-HTO sample, diffraction peaks of Ag_2O emerge and a peak at around 10° disappears. Figure 3 shows the XRD patterns of the ion exchanged samples using metal acetates. In the patterns of all samples, a diffraction peak (020) at around 10° indicating interlayer spacing was observed. The intensity ratio of the diffraction peak was changed by introducing various cations between the layers. This change is assumed to be due to a change of partial electron density and lattice constant by the introduced cation species between the layers. For Ag-HTO, Ag_2O emerges in the XRD pattern. A monovalent cation might be difficult to be included into

Table 2. Amount of ion exchanged cation by metal nitrate and acetate

cation	Metal nitrate/%	Metal acetate/%
Ca^{2+}	5	54
Mn^{2+}	9	86
Co^{2+}	10	76
Ni^{2+}	4	73
Cu^{2+}	20	77
Ag^+	56	100

Fig. 4. FT-IR spectra of the ion exchanged samples using metal nitrates.

the interlayer again. These XRD patterns show narrower diffraction lines than those of samples using metal nitrates. As a metal acetate is one of the salt of a weak acid, the layered titanate receives less damages than those by metal nitrate.

Table 2 shows amounts of ion exchanged cation using metal nitrate or acetate. In the case of metal nitrate, all samples except Ag-HTO shows small amounts about 20% or less. On the other hand, excluding the Ca-HTO, the amount shows a higher value of 70% or more for the samples using metal acetate. In the Ag sample, the reason for the large amount results from the formation of Ag_2O . The reason for the large amounts of cations by metal acetates will be difference between acid dissociation constants. The acid dissociation constants of nitric acids are higher than those of acetic acids. In other word, nitric acids tend to be dissociated more in aqueous solution. The equilibrium proceeds to the opposite side of dissociation by increasing proton for metal acetate. In the case of metal nitrates, the dissociated nitrate ion is difficult to consume the proton because nitric acids are strong. Consequently, metal acetate salts provide larger amounts of metal cations introduced. From the above results, we use a sample by metal acetates hereafter.

Figure 4 shows the FT-IR spectra of the ion exchanged samples using metal acetates. The peaks at around 3500 cm^{-1} and at around 1600 cm^{-1} are attributed to stretching and deformation vibration of H_2O in KBr, respectively. The peak at around 2400 cm^{-1} is antisymmetric stretching

vibration of C=O in CO₂ in the atmosphere. At smaller than 1000 cm⁻¹ range which is called a fingerprint region, Ti–O vibration can be observed.

3.2 Adsorption of Ammonia

Figure 5 shows the XRD patterns of the sample with ammonia adsorption via a liquid phase. The samples except for the Ag-HTO show slightly shift of the diffraction peak (020). Such shifts will result from formation of an ammonia complex with interlayer cations. On the other hand, Ag-HTO shows low crystallinity since the diffraction peak broadened and the diffraction peak (020) indicating the interlayer spacing could not be confirmed. **Figure 6** shows the FT-IR spectra of the sample with ammonia adsorption via an aqueous liquid phase. The peak at around 1300 cm⁻¹ emerges by ammonia adsorption. This peak is derived from symmetric deformation vibration of N–H in an ammonia molecule. These spectra confirm ammonia adsorption to the cation-intercalated layered titanates.

The amount of ammonia by an aqueous liquid phase was measured by CHN coder. The amounts were around

Fig. 5. XRD patterns of the sample with ammonia adsorption via aqueous liquid phase.

Fig. 6. FT-IR spectra of the sample with ammonia adsorption via aqueous liquid phase.

1.5–3.8 mass % for M-HTO, and 4.3 mass % for HTO. The plausible reason of the small amount of ammonia in the M-HTO samples is water coordination to metal cations in interlayer instead of ammonia. The ratio of adsorbed ammonia on exchanged cation can be calculated to around 0.4–1.6. In general, Mn²⁺, Co²⁺ and Ni²⁺ have six, Cu²⁺ has four and Ag⁺ has two ammonia ligands in the ammine complex.¹⁶⁾ For Ca²⁺, although there are few literatures for an ammine complex, a plausible value is eight ammonia ligands because of formation of CaCl₂·8NH₃.¹⁷⁾ The actual values in this paper are much lower than the theoretical ratio. In other words, there are some possibilities for increasing ammonia adsorption.

In the case of protonated sample, HTO-NH₃aq, a proton can be coordinated to an ammonia molecule to form an ammonium ion. According to the ratio of proton to ammonia is 1:1 in the ammonium ion, 64% of the proton was used for adsorption of ammonia. On the other hand, for example, the Ni-HTO sample shows only about 26% of the adsorption limit in the aqueous ammonia solution.

Figure 7 shows the temperature dependence of amount of fragmentation species with $m/z = 16, 17$ and 18 for Co-HTO-NH₃aq. From the TG-MASS, the peaks at 80°C were observed in the curve of $m/z = 17$ and 18 , and the peaks at around 230°C were observed in the curve of $m/z = 16$ and 17 . Generally, NH₃ species must be detected in the curve of $m/z = 16$ and 17 at an intensity ratio of approximately 4:5 while H₂O should show an intensity ratio of approximately 1:5 for $m/z = 17$ and 18 as showed in Table 1. Thus, the peak in $m/z = 18$ means H₂O, and that in $m/z = 16$ indicates NH₃ existence. In the curve of $m/z = 17$, both H₂O and NH₃ can be detected as a peak. Therefore, from the TG-MASS curve, H₂O will be desorbed at around 80°C and NH₃ at around 230°C, respectively. From these curves, intensity ratio of NH₃ ($m/z = 16$)/H₂O ($m/z = 18$) peaks can be calculated to around 0.31. Therefore, the amount of coordinated NH₃ may be smaller than H₂O. For the desorption temperature, the adsorbed ammonia in zeolite which has strong solid acidity have been reported at 400–700°C.¹⁸⁾ Our samples showed a relatively low temperature of about 230°C. Such

Fig. 7. Temperature dependence of amount of fragmentation species with $m/z = 16, 17$ and 18 for Co-HTO-NH₃aq samples.

Fig. 8. XRD patterns of MTO sample with ammonia adsorption via gas phase.

Fig. 9. Temperature dependence of amount of fragmentation species with $m/z = 16$, 17 and 18 for Co-HTO-NH₃gas samples.

low desorption temperature is achieved by adsorption of ammonia by forming an ammine complex with metal cations between layers, and possibly becomes a strong advantage for use of ammonia storage application.

In order to increase the amount of adsorption of ammonia, gas phase adsorption of ammonia was examined. **Figure 8** shows the XRD patterns for M-HTO sample with adsorption of ammonia by gas phase. These XRD patterns confirm that the diffraction peak of the interlayer spacing in a gas phase adsorption were slightly narrower than those by liquid phase adsorption. However, similar to the liquid phase adsorption, the (020) plane showing the layer structure in the Ag sample could not be observed. From this result, the sample except for the Ag-included one can adsorb ammonia while maintaining the layer structure.

Figure 9 shows the temperature dependence of amount of fragmentation species with $m/z = 16$, 17 and 18 for Co-HTO-NH₃gas. From this curve, intensity of the H₂O peak with $m/z = 18$ at 80°C decreased apparently. For NH₃, the peak ($m/z = 17$ and 18) shifted slightly to approx. 270°C. The intensity ratio for these peaks, NH₃/H₂O increased drastically to around 2.25. From these results, gas adsorp-

Fig. 10. Amounts of ammonia by aqueous liquid and gas phase.

tion is much effective than that in the aqueous solution for increase of adsorption amounts.

Figure 10 shows amounts of ammonia by liquid and gas phase. For HTO, the amounts of ammonia adsorption are similar for the samples by gas and liquid adsorption processes. However, M-HTO samples show two times better competency for adsorption of ammonia by gas phase than that by aqueous liquid phase. The reason of such increase of the amount of ammonia adsorption may be removal of water molecules coordinated to the metal cations between the layers by pretreatment. Consequently, M-HTO can adsorb more than 8 mass % of ammonia maximally using Ni-HTO. From the literatures, around 10 mass % of ammonia can be adsorbed reversibly.^{19),20)} Our materials show slightly smaller adsorption amount than the zeolites. However, exchange degree of Ni-HTO was only 73% as shown in Table 2. In addition, ammonia did not adsorb fully on Ni²⁺ for coordination number, 6. Actual mean coordination number can be estimated as around 4.8. Therefore, our material might have more competence for adsorption of ammonia. If Ni cation exchanges completely and ammonia can coordinate fully, the adsorption amount will be around 14 mass %. Thus, our material can be regarded as a potential candidate for ammonia adsorbing materials.

4. Conclusions

Lepidocrocite-type layered titanate was prepared by conventional solid-state reaction, and its protonation was carried out by introducing the lepidocrocite type layered titanate into 0.5 M hydrochloric acid. The protonation was accomplished with exchange degree of 97%.

Metal cations, Ca, Mn, Co, Ni, Cu and Ag, can be introduced into the interlayer gallery with ion exchange degree of 70% or larger using metal acetate. In the case of metal nitrate, ion exchange degree was 20% or less. Weaker acid salt will tend to be introduced into the interlayer space.

For the cation exchanged samples except for the Ag-HTO, the layered structure could be maintained after adsorption of ammonia. However, the composition ratio of metal cations and ammonia was apparently lower than the ideal ratio. The reason is plausibly due to the fact that water coordination reduces space for coordination of ammonia.

Adsorbed H₂O and NH₃ tend to desorb from the sample at around 80°C and 230–270°C. This result may be due to the adsorption of ammonia by forming an ammine complex with metal cations between layers. Such lower desorption temperature of ammonia can be strong advantage of the application. For example, these materials can be suggested to separate NH₃ from ammonia water (ammonia purification) by adsorption in aqueous solution and desorption by heating at 230–270°C.

The gas adsorption of ammonia was carried out and showed two times as much as the ammonia amounts of liquid phase adsorption. This result indicates that amount of ammonia can be possible to increase by removing water coordinated to cations between layer and adsorbing in a gas phase.

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