#### [Regular Paper]

# Ammonia Adsorption on Ion Exchanged Y-zeolites as Ammonia Storage Material

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Ammonia adsorption isotherm on ion exchanged Y-zeolites (Na-Y, H-Y, Co-Y, Cu-Y, K-Y, Rb-Y, and Cs-Y) was investigated to asses the potential for use in ammonia separation and storage, by measuring the adsorption isotherm at 323 to 473 K and below 1 atm.

Ammonia adsorption on Y-zeolite was increased by exchanging the cation with transition metal ions due to the increase in the number of ammonia adsorption sites with ammine complex formation, but was decreased by exchanging with alkali metal ions due to the decreased electrostatic attraction between ammonia and the zeolite surface. Irreversible ammonia adsorption sites on the ion exchanged Y-zeolite were classified into 3 types by IR (infrared) and TPD (temperature programmed desorption) techniques; M(OH)<sup>+</sup> (M: divalent cation), H<sup>+</sup>, and M<sup>+</sup> (M: alkali metal ion Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>). The first type of site bonds by ammonia adsorption with electrostatic attraction.

Cu<sup>2+</sup> exchanged Y-zeolite provided the best ammonia separation (4.92 mmol $\cdot$ g<sup>-1</sup>) with the temperature swing adsorption method (323-473 K, 40 kPa).

#### Keywords

Ammonia adsorption, Ion exchanged Y-zeolite, Ammonia storage, IR, TPD

# 1. Introduction

Our new de-NO<sub>x</sub> process with on-site ammonia synthesis proposed requires an ammonia adsorbent for separation and storage under 40-60 kPa of ammonia<sup>1</sup>). Our previous study of the behavior of ammonia adsorption on surface treated active carbon that the chemisorption site was oxygen on the surface. The strategy of surface design was investigated but the maximum ammonia separation capacity of H<sub>2</sub>SO<sub>4</sub> treated active carbon (H<sub>2</sub>SO<sub>4</sub>-AC) with the TSA (temperature swing adsorption) method was 2.58 mmol<sup>+</sup>g<sup>-1 2</sup>).

Ion exchanged zeolites are another possible ammonia adsorbent. The ion exchange is intended to increase the ammonia adsorption sites by ammonium ion formation or ammine complex formation<sup>3)~8)</sup>. However, the reported ammonia concentration<sup>3)~8)</sup> is too low (for example, 0.1 kPa) for our purpose.

The present study investigated the ion exchange effect on ammonia adsorption under a pressure of about

1 atm in six types of ion exchanged Y-zeolite (Co-Y, Cu-Y, H-Y, K-Y, Rb-Y, and Cs-Y), to assess the potential for use as an ammonia separation-storage material.

#### 2. Experimental Method

# 2.1. Sample Preparation and Characterization of Ion Exchanged Y-zeolite

Na form Y-zeolite (Na-Y; JRC-Y-5.6, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 5.6) and H form Y-zeolite (H-Y; JRC-HY-5.6, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 5.6) were used as the standard adsorbents of Y-zeolite. Metal (M: Co, Cu, K, Rb, Cs) ion exchanged Y-zeolites (M-Y) were prepared by exchanging Na-Y (5 g) with metal nitrate in aqueous solution (0.1 mol· $l^{-1}$ ; 200 ml) at 343 K for 3 h. Ion exchanged samples were washed with distilled water, dried in air at 383 K for overnight, and calcined in air at 773 K for 3 h. The composition of these ion exchanged Y-zeolites was determined by the XRF (X-ray fluorescence) measurement (EDX-800; Shimadzu, Ltd.). The BET surface area was measured by an automatic N<sub>2</sub> adsorption instrument (BELSORP 28SA; Bel Japan Co., Ltd.) at 77 K after evacuation at 723 K for 2 h.

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Sample	Surface area [m <sup>2</sup> ·g <sup>-1</sup> ]	SiO <sub>2</sub> [wt%]	Al <sub>2</sub> O <sub>3</sub> [wt%]	Na <sub>2</sub> O [wt%]	Metal oxide exchange [wt%]	Ion exchange [%] <sup>a)</sup>
Standard Y-zeoli	ite					
Na-Y <sup>b)</sup>	645	67.1	20.4	12.4		
$H-Y^{b)}$	566	72.8	22.0	3.5		
Transition metal	ion exchanged					
Co-Y	567	62.6	22.2	2.7	12.5 (CoO)	80.0
Cu-Y	542	62.3	21.9	1.8	14.0 (CuO)	86.5
Alkali ion excha	nged					
K-Y	555	60.7	21.7	1.1	16.5 (K <sub>2</sub> O)	91.7
Rb-Y	478	51.4	18.3	2.1	28.1 (Rb <sub>2</sub> O)	81.1
Cs-Y	396	41.5	15.8	2.1	40.6 (Cs <sub>2</sub> O)	78.1

a) Calculated from Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>.

b) Ref. 9.

# 2.2. Measurement of Ammonia Adsorption and Characterization of Irreversibly Adsorbed Ammonia

The ammonia adsorption isotherm was obtained by a volumetric method with a closed Pyrex glass system. The dry samples (100 mg) were placed in the Pyrex U-tube and then evacuated at 723 K for 2 h. The ammonia adsorption isotherm was measured between 0 kPa and 75 kPa at 323, 373, or 473 K. The ammonia adsorption isotherm was then measured again after evacuation to obtain the amount of irreversibly adsorbed ammonia.

The irreversibly adsorbed ammonia on the ion exchanged Y-zeolite was characterized by ammonia TPD (temperature programmed desorption) measurement and FT-IR (fourier transform infrared spectrometer) measurement. For ammonia TPD measurement, the dry sample (50 mg) was placed in a quartz U-tube, evacuated at 873 K for 1 h, and cooled down to 373 K. After ammonia pre-adsorption for a few minutes, the sample was evacuated for 30 min to remove the physisorbed ammonia. Ammonia TPD was carried out in He flow (100 ml·min<sup>-1</sup>), with a temperature increase rate of 10 K·min<sup>-1</sup> between 373 K and 873 K. Desorbed ammonia was directly detected by a TCD (thermal conductivity detector).

For FT-IR measurement, the dry sample disk (150 mg) was set in the IR cell, evacuated at 873 K for 1 h, and cooled down to 373 K. After the background IR spectrum was measured, ammonia was adsorbed on the sample at 373 K for 15 min. IR measurement (FT/IR-350; JASCO Co., Ltd.) was carried out at 373 K after evacuation for 30 min at 373, 523, and 673 K, respectively.

### 3. Results and Discussion

# 3. 1. Sample Composition of Ion Exchanged Y-zeolite

The surface area and the composition of the ion

exchanged Y-zeolites are shown in **Table 1**<sup>9)</sup>. The ion exchange degree, calculated from the ratio of  $Na_2O/Al_2O_3$ , are also shown in **Table 1**.

# 3. 2. Effect of Ion Exchange in Y-zeolite on Ammonia Adsorption

Ammonia adsorption was characterized for Na-Y and the six types of ion exchanged Y-zeolites. The amounts of total, irreversible, and reversible ammonia adsorption under standard condition (40 kPa, 323-473 K) are summarized in **Table 2**.

### 3. 2. 1. Transition Metal Ion Exchanged Y-zeolite

The characteristics of ammonia adsorption of transition metal ion exchanged Y-zeolites measured at 323 K are shown in **Fig. 1**. Transition metal ion exchange in Na-Y increased ammonia adsorption compared with Na-Y indicating that the number of ammonia adsorption sites is increased by transition metal ion exchange. The interaction between ammonia and transition metal ion exchanged Y-zeolite is discussed in the next section.

**Tables 1** and **2** summarize the surface area and ammonia adsorption at 40 kPa, respectively. Transition metal ion ( $Co^{2+}$ ,  $Cu^{2+}$ ) exchange to Y-zeolite increased both reversible and irreversible adsorption. The ratio of reversible adsorption to total adsorption for H-Y was equal to that for Na-Y. However, absolute value of ammonia adsorption on H-Y is lower than that on Na-Y indicating that the interaction between ammonia and H-Y is similar to that for Na-Y. The decrease of adsorption is caused by the decrease in surface area.

### 3. 2. 2. Alkali Metal Ion Exchanged Y-zeolite

The characteristics of ammonia adsorption on alkali metal ion exchanged Y-zeolites measured at 323 K are shown in **Fig. 2**. Alkali metal ion exchange to Na-Y decreased ammonia adsorption due to the weaker interaction between ammonia and alkali ion exchanged Yzeolite compared to Na-Y, or due to the decrease in surface area.

Alkali ion ( $K^+$ ,  $Rb^+$ , or  $Cs^+$ ) exchanged Y-zeolites had drastically decreased irreversible adsorption as

Table 2 Ammonia Adsorption on Ion Exchanged Y-zeolite at 40 kPa

Sample	$\begin{array}{c} 323 \ K^{a)} \\ total^{b)} \\ [mmol \cdot g^{-1}] \end{array}$	Reversible <sup>c)</sup> [mmol·g <sup>-1</sup> ]	Irreversible <sup>d)</sup> [mmol·g <sup>-1</sup> ]	Rev./Total	$\begin{array}{c} 373 \ K^{a)} \\ total^{b)} \\ [mmol \cdot g^{-1}] \end{array}$	$\begin{array}{c} 473 \ K^{a)} \\ total^{b)} \\ [mmol \cdot g^{-1}] \end{array}$
Na-Y	6.14	5.00	1.14	0.81	4.24	2.08
K-Y	6.06	5.83	0.23	0.96	4.31	1.89
Rb-Y	5.01	4.83	0.18	0.96	3.73	1.56
Cs-Y	4.59	4.54	0.05	0.99	3.21	1.39
H-Y	5.44	4.37	1.07	0.80	3.60	1.61
Co-Y	8.64	7.03	1.61	0.81	6.81	4.42
Cu-Y	9.34	6.49	2.85	0.69	7.85	4.42

a) Adsorption temperature.

b) Adsorption at 1st measurement.

c) Adsorption at 2nd measurement.

d) Difference between total adsorption and reversible adsorption.



 $(\bigcirc,\bigcirc)$  Na-Y,  $(\blacktriangle,\bigtriangleup)$  H-Y,  $(\blacksquare,\Box)$  Co-Y,  $(\diamondsuit,\diamondsuit)$  Cu-Y.

Fig. 1 Adsorption Isotherm of Ammonia (closed symbol: first measurement; open symbol: second measurement) on Transition Metal Ion Exchanged Y-zeolites at 323 K

shown in **Fig. 2. Figure 3** shows IR spectra of adsorbed ammonia on Na-Y, K-Y, Rb-Y and Cs-Y after evacuation at 373 K. The IR peak of Na-Y at  $1631 \text{ cm}^{-1}$  disappeared after ion exchange with K<sup>+</sup>, Rb<sup>+</sup>, or Cs<sup>+</sup>, but no other IR peaks appeared, indicating that ammonia adsorption is reduced by ion exchange from Na<sup>+</sup> to K<sup>+</sup>, Rb<sup>+</sup>, or Cs<sup>+</sup>. These observations indicate that ammonia adsorption on alkali ion exchanged Y-zeolites is weaker than adsorption on Na-Y.

# 3.3. Irreversible Ammonia Adsorption on Ion Exchanged Y-zeolite

Irreversible adsorption of ammonia on Na-Y, H-Y, Co-Y, and Cu-Y was characterized by ammonia TPD and FT-IR measurements.

Figure 4 shows the TPD profiles of irreversibly adsorbed ammonia on Na-Y, H-Y, Co-Y, and Cu-Y,



Fig. 2 Adsorption Isotherm of Ammonia (closed symbol: first measurement; open symbol: second measurement) on Alkali Ion Exchanged Y-zeolites at 323 K

and **Table 3** lists the desorption peak temperatures. **Figure 5** shows IR spectra of adsorbed ammonia on Na-Y, H-Y, Co-Y, and Cu-Y as a function of desorption temperature, and **Table 4** lists the peak assignments.

Na-Y had only one desorption peak at 485 K, and the corresponding IR peak at 1631 cm<sup>-1</sup> disappeared after evacuation at 523 K. The irreversibly adsorbed ammonia presumably bonded by electrostatic attraction between Na<sup>+</sup> and the lone electron pair of ammonia.

H-Y has two desorption peaks at 508 K and 550 K. The IR peak at 1619-1623 cm<sup>-1</sup> was diminished at 523 K and the peak at 1449 cm<sup>-1</sup> disappeared after evacuation at 673 K. H-Y has two ammonia adsorption sites, un-exchanged Na<sup>+</sup> and H<sup>+</sup>. Considering the results of Na-Y, the desorption peak at 508 K and IR peak at



Fig. 3 IR Spectra of Irreversibly Adsorbed Ammonia on Alkali Ion Exchanged Y-zeolites after Evacuation at 373 K



Fig. 4 TPD Spectra of Ammonia on Ion Exchanged Y-zeolites

1619-1623 cm<sup>-1</sup> were assigned to ammonia on unexchanged Na<sup>+</sup> sites, and the desorption peak at 550 K and IR peak at 1449 cm<sup>-1</sup> is to ammonium ion (NH<sub>4</sub><sup>+</sup>) formation with H<sup>+</sup> sites<sup>10)~12</sup>.

TPD for Co-Y showed three desorption peaks at 507, 565, and 787 K, suggesting the presence of three types of adsorption site. The ion exchange reaction of Na form zeolite with divalent cations is expressed as fol-



(a) Na-Y, (b) H-Y, (c) Co-Y, (d) Cu-Y.

Fig. 5 IR Spectra of Irreversibly Adsorbed Ammonia on Ion Exchanged Y-zeolites after Evacuation at 373, 523, and 673 K

lows<sup>13)</sup>:

$$2ZO^{-}Na^{+} + M^{2+} + H_2O$$

$$\longrightarrow ZO^{-}H^{+} + ZO^{-}M(OH)^{+} + 2Na^{+}$$

 $\longrightarrow$  ZO<sup>-</sup>H<sup>+</sup> + ZO<sup>-</sup>M(OH)<sup>+</sup> + 2Na<sup>+</sup> (1) Thus, the ammonia adsorption sites of Co-Y are unexchanged Na<sup>+</sup>, H<sup>+</sup>, and Co(OH)<sup>+</sup>. From the results of Na-Y and H-Y, the desorption peak at 507 K and IR peak at 1633 cm<sup>-1</sup> can be assigned to ammonia on unexchanged Na<sup>+</sup>, and the desorption peak at 565 K and IR peak at 1529-1549 cm<sup>-1</sup> to ammonium ion. Therefore, the desorption peak at 787 K and IR peak at 1605-1614 cm<sup>-1</sup> can be assigned to ammonia on Co(OH)<sup>+</sup> (Co ammine complex formation).

Table 3 Summary of Ammonia TPD Spectra for Ion Exchanged Y-zeolite

Sampla	Temperature of	Temperature of	Temperature of	Total amount
Sample	[K]	[K]	[K]	[mmol·g <sup>-1</sup> ]
Na-Y	485			0.97
H-Y	508	550		1.03
Co-Y	507	565	787	2.79
Cu-Y		526		3.65

Sample	Suggested	IR peak [cm <sup>-1</sup> ] of ammonia on the sample evacuated at				
	sites	373 K	523 K	673 K		
Na-Y	Na <sup>+</sup>	1631				
H-Y	Na <sup>+</sup>	1619	(1623)			
	$H^+$	1449	1449			
Co-Y	Na <sup>+</sup>	1633				
	Co(OH)+	1605	1614	1614		
	$H^+$	1529	1549			
Cu-Y	Na <sup>+</sup>	1624				
	Cu(OH)+	1604	1615			
	H+	1443	1443			

Table 4 Suggested Sites of Ammonia Adsorption on Ion Exchanged Y-zeolite Based on the IR Spectra



Fig. 6 Model of Ammonia Adsorption on Ion Exchanged Y-zeolites

Cu-Y had only one TPD peak at 526 K, but three IR peaks after evacuation at 373 K, suggesting that there are three ammonia adsorption sites on Cu-Y, but the three TPD peaks overlap. The IR peak at  $1624 \text{ cm}^{-1}$  can be assigned to ammonia on Na<sup>+</sup>,  $1443 \text{ cm}^{-1}$  to ammonium ion, and  $1604-1615 \text{ cm}^{-1}$  to ammonia on Cu(OH)<sup>+</sup> (Cu ammine complex formation). These results show that irreversibly adsorbed ammonia present as the ammine complex is more strongly bound than ammonia on Na<sup>+</sup> sites<sup>11),12),14</sup>). This observation also agrees with the data from the isotherm measurements; the ratio of reversible adsorption to total adsorption for Cu-Y is lower than for Na-Y.

M<sup>2+</sup> sites may appear after exchanging divalent ions with high Al content zeolite such as Y-zeolite:

$$2ZO^{-}Na^{+} + M^{2+} \longrightarrow (ZO^{-})_2M^{2+} + 2Na^{+}$$
(2)

 $M^{2+}$  sites and  $M(OH)^+$  sites are difficult to distinguish based on TPD and IR measurements, but the amount of  $M^{2+}$  sites is probably lower than that of  $M(OH)^+$  sites because of the difficulty of charge duplication.

The solid state NMR method can detect other types of weakly adsorbed species, with hydrogen bonding to previously adsorbed ammonia in the presence of free ammonia molecules<sup>10</sup>. However, our IR measurements after evacuation could detect no such species.

3.4. Ammonia Adsorption Mechanism and the Involvement of Adsorption Sites on Ion Exchanged Y-zeolite

Figure 6 proposes a model of irreversible ammonia

adsorption on ion exchanged Y-zeolites. Na<sup>+</sup> is present as an exchangeable cation on Na-Y (**Fig. 6** (a)). Ammonia can be adsorbed on Na-Y by electrostatic attraction with Na<sup>+</sup> ions (**Fig. 6** (b)).

Transition metal ion exchange results in a part of the Na<sup>+</sup> being replaced with M(OH)<sup>+</sup> and H<sup>+</sup> as shown in reaction 1 (Fig. 6 (c)). Ammonia is then adsorbed on M(OH)<sup>+</sup> with formation of the ammine complex  $(M(NH_3)_x(OH)^+)$ , on  $H^+$  with formation of ammonium ion, and on un-exchanged Na<sup>+</sup> by electrostatic attraction (Fig. 6(d)). The stoichiometry, x, between M(OH)<sup>+</sup> and coordinated ammonia can be roughly calculated from the ion exchange degree and the amount of irreversibly adsorbed ammonia per unit area with the following assumptions: all exchanged ions contribute to irreversible adsorption, the number of H+ sites and M(OH)<sup>+</sup> sites are equal, and the stoichiometry between H<sup>+</sup> and ammonia is equal to 1. The values of x for Co-Y and Cu-Y are thus estimated to be 2.2 and 5.0, respectively.

Alkali ion exchange results in a part of the Na<sup>+</sup> being replaced by alkali ion (K<sup>+</sup>, Rb<sup>+</sup>, or Cs<sup>+</sup>) (**Fig. 6** (e)). Ammonia is adsorbed on the exchanged alkali ion and un-exchanged Na<sup>+</sup> by electrostatic attraction (**Fig. 6** (f)). The ratio of irreversibly adsorbed ammonia to total adsorbed ammonia for alkali metal ion exchanged Y-zeolites was lower than that for Na-Y, indicating that the electrostatic attraction between these alkali ion and ammonia is weaker than that between Na<sup>+</sup> and ammonia, due to the increase in monovalent cation radius from Na<sup>+</sup> to K<sup>+</sup>, Rb<sup>+</sup>, or Cs<sup>+</sup>.

The mechanism of reversible adsorption is related with that of irreversible adsorption. A sample with high irreversible adsorption adsorbs much ammonia as the total adsorption as shown in **Table 2**.

# 3.5. Application of Ion Exchanged Y-zeolite to TSA and PSA in Ammonia Separation

Ammonia separation with the TSA method between 323 K adsorption temperature and 473 K desorption temperature at 40 kPa, and that with the PSA (pressure swing adsorption) method between 40 kPa adsorption pressure and 10 kPa desorption pressure are summarized in **Fig. 6**<sup>1)</sup>. Ammonia separation with TSA was defined as the difference in total adsorption at 323 K and 473 K<sup>15)</sup>. Ammonia desorption at 473 K was selected to allow for the utilization of waste heat from ammonia synthesis (at 623 K). Ammonia separation with PSA was defined as the difference in reversible adsorption between 40 kPa and 10 kPa<sup>15)</sup>. Samples with higher surface area showed better performance.

Ammonia separation with the TSA method using ion exchanged Y-zeolites is higher than that using surface treated active carbon, and transition metal ion exchanged Y-zeolites showed higher performance. Samples with high irreversible adsorption showed better performance. In particular, the separation capacity



Fig. 7 Ammonia Separation on Ion Exchanged Y-zeolites and Surface Treated Active Carbon (H<sub>2</sub>SO<sub>4</sub>-AC; previously reported data<sup>1</sup>) Using the Temperature Swing Adsorption (■) and Pressure Swing Adsorption (□) Methods

of Cu-Y was 4.92 mmol $\cdot$ g<sup>-1</sup>, higher than the H<sub>2</sub>SO<sub>4</sub>-AC (2.58 mmol $\cdot$ g<sup>-1</sup>) previously reported<sup>2</sup>). Therefore, the amount of ammonia separation material can be decreased to 40% of the previously proposed adsorbent (H<sub>2</sub>SO<sub>4</sub> treated active carbon; 1.75 mmol $\cdot$ g<sup>-1</sup> of separation capacity)<sup>1</sup>.

Ammonia separation with the PSA method was in the range of 0.87 mmol $\cdot$ g<sup>-1</sup> (Cs-Y)-1.43 mmol $\cdot$ g<sup>-1</sup> (H-Y), which were similar to the values for surface treated active carbon of 1.18 mmol $\cdot$ g<sup>-1</sup> (HNO<sub>3</sub> treated active carbon)-1.32 mmol $\cdot$ g<sup>-1</sup> (H<sub>2</sub>SO<sub>4</sub> treated active carbon)<sup>2</sup>). Therefore, surface treated active carbon (oxidized active carbon) is more cost effective than ion exchanged Y-zeolite for the PSA method.

# 4. Conclusion

Investigation of the behavior of ammonia adsorption on ion exchanged Y-zeolites (Na-Y, H-Y, Co-Y, Cu-Y, K-Y, Rb-Y, and Cs-Y) showed the following.

Ammonia adsorption on transition metal ion exchanged Y-zeolites (Co-Y, Cu-Y) was higher than on Na-Y due to the increase in ammonia adsorption sites with ammine complex and ammonium ion formation. On the other hand, adsorption on alkali metal ion exchanged Y-zeolites (K-Y, Rb-Y, Cs-Y) was lower than on Na-Y due to the decrease of electrostatic attraction between ammonia and the zeolite surface.

Ammonia adsorption sites on ion exchanged Y-zeolite could be classified into 3 types;  $M(OH)^+$  (M: divalent cation), H<sup>+</sup>, and M<sup>+</sup> (M: alkali metal ion Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>).

Cu-Y provides the ammonia best separation with the

TSA method between 323 K and 473 K at 40 kPa (4.92 mmol  $\cdot$  g<sup>-1</sup>) among the zeolites in this study.

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要 旨

# アンモニア貯蔵材料としてのイオン交換 Y ゼオライトへのアンモニア吸着

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323~473 K における 1 atm 以下のアンモニアの分離貯蔵を目 的として,7種類のイオン交換 Y ゼオライト (Na, H, Co, Cu, K, Rb, Cs 型)のアンモニア吸着挙動の検討を行った。

Na型Y ゼオライトを遷移金属でイオン交換することにより アンモニア吸着量は増大したが、アルカリ金属でイオン交換す ることによって吸着量は減少した。アンモニアの不可逆吸着状 態を赤外分光法・昇温脱離法によって分析し、3種類 [M(OH)+ (M: 2 価陽イオン), H+, M+ (M: アルカリ金属イオ ン)]のアンモニア吸着サイトを同定し, それぞれアンミン錯 体形成, アンモニウムイオン形成, 静電引力によるアンモニア 吸着の寄与によるものと考察した。

温度スイング法 (323~473 K, 40 kPa) によるアンモニア分 離容量は, Cu型Y ゼオライトが最高性能 (4.92 mmol·g<sup>-1</sup>) を 示した。

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