Absorption and Desorption Behavior of Ammonia with Alkali Earth Halide and Mixed Halide

Chun Yi Liu and Ken-ichi Aika*
Department of Environmental Chemistry and Engineering, Interdisciplinary Graduate School of Science and Engineering,
Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa 226-8502

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Alkali earth metal halides were studied for the use as ammonia storage material operated below 60 kPa. Reversible and irreversible absorption were observed for each samples. $MgCl_2$, $CaCl_2$, and $CaBr_2$ were found to be adequate for TSA method (between 298 and 473 K), and these storage capacities were much higher than that of Na–Y zeolite. $CaCl_2$–$CaBr_2$ mixed halides proved to be a useful material with large absorption for PSA cycling between 10 and 60 kPa of ammonia.

Ammonia production can be possible under mild condition such as 623 K and 10 bar with the development of second-generation ammonia catalysts; promoted ruthenium catalysts. Under these conditions, produced ammonia with pressure of 40–60 kPa must be separated. If any effective ammonia absorber is developed, small scale ammonia production can be practical and used for many purposes, such as de-NOx process.[1] However, any materials for ammonia separation and storage for such a purpose have not been utilized practically, because of the low ammonia storage capacity.

The ammonia adsorption and desorption behavior of surface treated active carbon and ion exchanged Y-zeolites have been studied, however, the ammonia storage capacity of these materials are not high.[2] The successful ammonia storage material must have high capacity under 40–60 kPa of ammonia at ambient temperature, and must release ammonia easily by a mild operation such as evacuation to 10 kPa (pressure swing adsorption: PSA) or heating to 473 K (temperature swing adsorption: TSA). The ammonia absorption behavior of $CaCl_2$ has been reported for the chemical heat pump use,[3,4] however, the pressure is much higher than that of our purpose.

Here, ammonia absorption and desorption behavior of five kind of alkali earth metal halides ($MgCl_2$, $CaCl_2$, $CaBr_2$, $SrCl_2$, and $SrBr_2$) and three kind of $CaCl_2$–$CaBr_2$ mixed halides were studied under pressure below 80 kPa, maximum ammonia pressure under the synthesis condition above written.

The alkali earth metal halide hydrate was used as the starting compound. The powder samples were pressed, crushed, and sieved to 2 mm grains. $CaCl_2$ and $CaBr_2$ were mixed in aqueous solution, and dried at 383 K.[4] The solid samples were crushed and sieved to 2 mm grains.

Ammonia absorption and desorption isotherms were measured between 0 and 80 kPa at 298 and 473 K after evacuation at 523 K as pretreatment. The measurement was carried out with OMNISORP 100CX (Beckman Coulter). Amount of absorbed ammonia was calculated from the pressure change. When the pressure change in 40 s became smaller than 26.7 Pa (0.2 Torr), the absorption was considered as equilibrium. About 10 min was necessary to obtain one point. Ammonia absorption and desorption isotherms were measured for two times. Adsorbed amount at the first measurement was denoted as the total absorption. The sample was evacuated to remove (reversibly absorbed) ammonia at the same temperature for 1 h, then the second (reversible) absorption and desorption measurement was carried out.

The total ammonia absorption isotherms of alkali earth metal halides and ammonia coordination number to these samples are shown in Figure 1 together with Na form Y-zeolite (as reference). Sample weight was defined as the sample amount after pretreatment. From the results of XRD and TG/DTA analysis, the dehydration of $MgCl_2$ was not complete, and the hydration number of it was approximately 1. Thus, the molecular weight of 113.19 (Mw of $MgCl_2 \cdot H_2O$) was used for the calculation of ammonia coordination number. On the other hand, the dehydration of other samples was approximately completed. Coordination number N shown in Figure 1 is the value for $CaCl_2$ sample. For the other samples, the coordination number is calculated as $N \cdot f$ (conversion factor). The conversion factor f calculated from the molecular weight of the sample is shown in the figure caption. The ammonia absorption behavior is classified into three groups. $MgCl_2$, $CaBr_2$, and $SrBr_2$ absorbed ammonia even below 10 kPa, and $CaCl_2$ absorbed ammonia beyond 30 kPa stepwise. The ammonia absorption capacities of these two groups under 40 or 60 kPa were higher than that of Na form Y-zeolite remarkably. The last sample, $SrCl_2$, absorbed ammonia above 70 kPa. $SrCl_2$ does not meet with the condition shown above.[5]

The storage capacity with TSA method was estimated as the

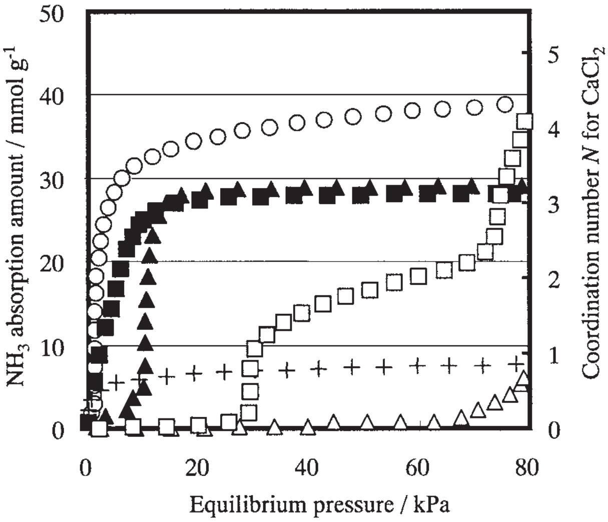

Figure 1. Total absorption isotherm and coordination number N of ammonia measured at 298 K; (○) $MgCl_2$ ($f = 1.02$), (□) $CaCl_2$ ($f = 1.00$), (■) $CaBr_2$ ($f = 1.80$), (△) $SrCl_2$ ($f = 1.43$), (▲) $SrBr_2$ ($f = 2.23$), and (+) Na–Y zeolite. f is the conversion factor of N.

difference in total absorption amount between 298 and 473 K at 40 kPa. The capacity was 26 for $MgCl_2$, 14 for $CaCl_2$, 23 for $CaBr_2$, 0.6 for $SrBr_2$, and 4.7 mmol-NH_3 g^{-1} for Na^+ form Y-zeolite, respectively. Ammonia desorption temperature of 473 K was selected from the viewpoint of utilization of produced heat from ammonia synthesis. The storage capacity of $MgCl_2$, $CaCl_2$, and $CaBr_2$ were higher than Na form Y-zeolite, and then these samples are applicable for ammonia storage material with TSA method.

The reversible (second) ammonia absorption and desorption isotherms with alkali earth metal halide were measured, and the results are shown in Figure 2. $CaCl_2$ absorbed ammonia above 30 kPa for the first run (Figure 1), however, it started to absorb it above 75 kPa at the second run. $MgCl_2$ and $CaBr_2$ had similar absorption behavior for first (Figure 1) and second (Figure 2) run respectively, but the amount was low at the second run. These halides could not desorb ammonia reversibly at 10 kPa or above.

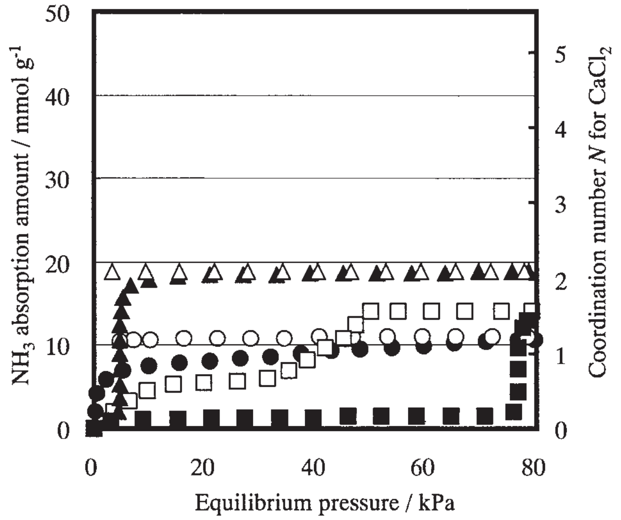

Figure 2. Reversible absorption isotherm (closed symbol) and desorption isotherm (open symbol) and coordination number N of ammonia measured at 298 K; (●, ○) $MgCl_2$ ($f = 1.02$), (■, □) $CaCl_2$ ($f = 1.00$), and (▲, △) $CaBr_2$ ($f = 1.80$). f is the conversion factor of N.

The similar reversible absorption experiments were carried out for $CaCl_{1.33}Br_{0.67}$, $CaClBr$, and $CaCl_{0.67}Br_{1.33}$, and the results are shown in Figure 3. With mixing of Br ion to $CaCl_2$, ammonia reversible absorption started below 60 kPa, and drastic (reversible) desorption was observed above the pressure of 10 kPa.

Now the results are compared under the condition of PSA cycle between 60 kPa (absorption pressure) and 10 kPa (desorption pressure) at 298 K. The capacity of alkali earth metal halides was 0.0 for $CaCl_2$, 26 for $CaCl_{1.33}Br_{0.67}$, 16 for $CaClBr$, 13 for $CaCl_{0.67}Br_{1.33}$, and 0.0 mmol-NH_3 g^{-1} for $CaBr_2$, respectively. For pure alkali earth metal halides, ammonia which has been absorbed at 60 kPa can not desorb at 10 kPa (Figure 2). Therefore, these samples are not applicable for PSA method with pressure cycle between 60 and 10 kPa. On the other hand, $CaCl_2$–$CaBr_2$ mixed halides which have absorbed ammonia at 60 kPa can desorb it at 10 kPa. Therefore, these samples can be applicable for ammonia storage material with PSA method.

The ammine complex of $CaCl_2(NH_3)_2$ and $CaBr_2(NH_3)_2$ are stable under evacuated condition during ammonia absorption and desorption measurement.[6,7] Then, the reversible ammine complex formations for these materials occur at some ammonia pressure such as 40 or 60 kPa.[8] Interaction of ammonia and alkali earth metal halide is ammine complex formation (and decomposition) through ligand exchange between halogen and ammonia with structure change. The structure of $CaCl_2$ is rutile type, thus 6 atoms of Cl^- is coordinated to Ca^{2+}. By the complex formation to $CaCl_2(NH_3)_2$, the coordination number of Cl^- is changed from 6 to 4 and 2 molecules of NH_3 is coordinated to Ca^{2+}. For the complex formation to $CaCl_2(NH_3)_8$, 6 molecules of NH_3 is coordinated to Ca^{2+}, and 2 molecules of NH_3 and 2 ions of Cl^- exist in the surrounding space of $[Ca(NH_3)_6]^{2+}$.[8] The reactivity against ammonia is higher for $CaBr_2$ than for $CaCl_2$ (Figure 1 and 2), and it can be understood with the spectrochemical series: stability with ligand ($Br^- < Cl^- < NH_3$).

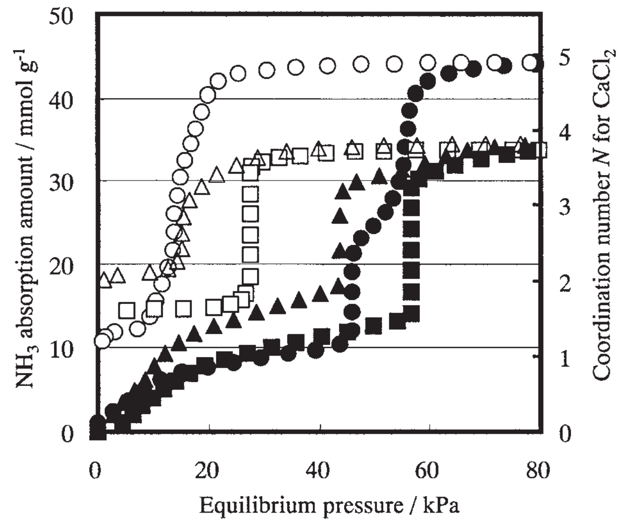

Figure 3. Reversible absorption isotherm (closed symbol) and desorption isotherm (open symbol) and coordination number N of ammonia measured at 298 K; (●, ○) $CaCl_{1.33}Br_{0.67}$ ($f = 1.27$), (■, □) $CaClBr$ ($f = 1.40$), and (▲, △) $CaCl_{0.67}Br_{1.33}$ ($f = 1.53$). f is the conversion factor of N.

It is concluded that $MgCl_2$, $CaCl_2$, $CaBr_2$, and $SrBr_2$ are useful for ammonia storage material with TSA and $CaCl_2$–$CaBr_2$ mixed halides are useful with PSA. The mixing of different halogens in alkali earth metal halide is effective for controlling ammonia absorption and desorption behavior.

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