Reversible ammonia uptake at room temperature in a robust and tunable metal–organic framework†

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Ammonia is useful for the production of fertilizers and chemicals for modern technology, but its high toxicity and corrosiveness are harmful to the environment and human health. Here, we report the recyclable and tunable ammonia adsorption using a robust imidazolium-based MOF (JCM-1) that uptakes 5.7 mmol g⁻¹ of NH₃ at 298 K reversibly without structural deformation. Furthermore, a simple substitution of NO₃⁻ with Cl⁻ in a post-synthetic manner leads to an increase in the NH₃ uptake capacity of JCM-1(Cl⁻) up to 7.2 mmol g⁻¹.

Metal–organic frameworks (MOFs) have emerged as a promising material for the capture of toxic chemicals such as NH₃, NO₃⁻, SO₂, and volatile organic compounds because well-ordered porosity with feasible chemical and structural tunability of pore surfaces enables such applications. Synthesis of MOFs with high structural stability toward corrosive species is a critical issue for real-world applications. In this regard, several MOFs that can take up NH₃ under atmospheric conditions has been developed recently. Nevertheless, structural instability of adsorbent and high regeneration temperature are still remaining challenges for practical applications.

Introduction

Ammonia is one of the essential chemicals not only for fertilizers in agriculture but also for various industrial applications such as an alternative fuel, refrigerants, and a precursor for numerous nitrogenous compounds. As the second most-produced chemical in the world, over 150 million tons of ammonia is annually produced. Such a huge production and extensive usage of NH₃ raises concerns about the environment and human health issues because of its toxic and corrosive properties. The United States Department of Labor alerts that exposure only to a small amount of ammonia can damage a human body. In the atmosphere, NH₃ can combine with sulfate and nitrate to form fine particulate matter (PM2.5), causing severe particulate air pollution. In this context, practical methods and materials for the removal of ammonia emitted in the air are highly desirable.

Metal–organic frameworks (MOFs) have emerged as a promising material for the capture of toxic chemicals such as NH₃, NO₃⁻, SO₂, and volatile organic compounds because well-ordered porosity with feasible chemical and structural tunability of pore surfaces enables such applications. Synthesis of MOFs with high structural stability toward corrosive species is a critical issue for real-world applications. In this regard, several MOFs that can take up NH₃ under atmospheric conditions has been developed recently. Nevertheless, structural instability of adsorbent and high regeneration temperature are still remaining challenges for practical applications.

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Results and discussion

Synthesis and characterization of JCM-1 and JCM-1(Cl\(^{–}\))

Herein, we report the recyclable and tunable ammonia adsorption using JCM-1, which is the first demonstration of NH\(_3\) capture utilizing an imidazolium-based MOF. JCM-1 was synthesized according to the previous procedure by heating a mixture of Co(NO\(_3\))\(_3\)(H\(_2\)O)\(_6\) and the H\(_2\)PzImCl ligand in N,N-dimethylformamide (details in the ESIF). In the single-crystal X-ray structure of JCM-1, one-dimensional channels are running through the [001] direction with an aperture size of 12.5 \(\times\) 3.9 \(\AA\). The nitrate anion in the channels of JCM-1 can be fully replaced by chloride ion to obtain JCM-1(Cl\(^{–}\)) by post-synthetic anion exchange method following the previous procedures. The crystal structure of JCM-1(Cl\(^{–}\)) by single-crystal X-ray diffraction analysis showed that the space group of JCM-1(Cl\(^{–}\)) was not changed (P4\(_{1}\)/amd) with almost the same unit cell parameters as JCM-1 (Fig. S2 and Table S1\(^{†}\)); the cationic scaffold remained unchanged, and only the anion species in the pore was replaced after ion substitution. When the crystals of JCM-1 were treated with 1 M ammonia solution in THF for 24 hours (Fig. 2a), the crystals remained intact, which secures the chemical stability of JCM-1 toward corrosive ammonia, enabling NH\(_3\) gas uptake measurements.

The total NH\(_3\) uptake amounts of JCM-1 at 1 bar were 7.9 and 5.7 mmol g\(^{–}\)\(^1\) at 273 K and 298 K, respectively (Fig. 2b), which are comparable with other NH\(_3\) adsorbing MOFs.\(^{5,19,20}\) Notably, JCM-1 surpasses other materials in terms of framework stability upon regeneration, which are the critical properties of energy-efficient NH\(_3\) adsorbent materials. Although a substantial number of MOFs were tested for ammonia adsorption thus far, they suffer from structural deformation after exposure to corrosive NH\(_3\) gas.\(^{5,7–9,19,41}\) Many of the MOFs show decreased porosity with the degradation of crystallinity during repeated NH\(_3\) adsorption–desorption processes, resulting in peak broadening in powder X-ray diffraction (PXRD) patterns. In contrast, JCM-1 could maintain the initial crystallinity and the porosity after NH\(_3\) adsorption experiments, which was confirmed by the almost unchanged PXRD patterns and N\(_2\) sorption isotherms (Fig. 2c and d).

Fig. 2 (a) A picture for the crystals of JCM-1 stored in 1 M ammonia THF solution at room temperature for 24 hours. (b) NH\(_3\) adsorption isotherms of JCM-1 at 273 K and 298 K. (c) PXRD patterns and (d) N\(_2\) adsorption isotherms of JCM-1 before and after ammonia adsorption experiments (black circle, before NH\(_3\) sorption; light-green circle, after NH\(_3\) sorption).

Ammonia adsorption of JCM-1 and JCM-1(Cl\(^{–}\))

Unlike other MOFs capturing ammonia, JCM-1 has no open metal sites and no acid functional groups for strong interaction with NH\(_3\). Instead, it possesses imidazolium functional groups on the pore surfaces to form weak hydrogen bonds with NH\(_3\), enabling NH\(_3\) capture utilizing an imidazolium-based MOF.

Fig. 1 Schematic illustration of ammonia adsorption with JCM-1 and JCM-1(Cl\(^{–}\)).
The imidazolium protons and counter anions in JCM-1 can act respectively as a proton donor and a proton acceptor, enabling cooperative hydrogen bonding with NH₃. This weak but effective intermolecular interaction seems to facilitate the re-activation of JCM-1 after repeated NH₃ adsorption measurements. We carried out cycle experiments (Fig. 4a and c), and observed that the sample could be fully evacuated at room temperature under dynamic vacuum. The NH₃ uptake capacity was well retained over five cycles, showing the facile regenerability of JCM-1 under mild conditions.

The NH₃ uptake capacity and sorption affinity of JCM-1 could be also modulated by replacing NO₃⁻ with Cl⁻ in a post-synthetic manner, where JCM-1 was soaked in a methanol solution of LiCl for a week to give anion-exchanged JCM-1(Cl⁻). Although the effectiveness of anion inserted into a MOF for modulating ammonia uptake was reported by Binaeian,¹⁵ the exchange of counter anions in the cationic framework was investigated for ammonia uptake in our case. The NH₃ uptake capacity of JCM-1(Cl⁻) was increased, although its N₂ adsorption behavior was almost the same (Fig. 3). Because of high porosity of JCM-1 and the weaker interaction with nitrogen compared to ammonia, the anion exchange effect on the nitrogen adsorption properties of JCM-1 and JCM-1(Cl⁻) is less pronounced compared to the ammonia adsorption. At 1 bar, JCM-1(Cl⁻) adsorbed 11.7 and 7.2 mmol g⁻¹ of NH₃ at 273 K and 298 K, respectively, which increased by 48% (273 K) and 26% (298 K), compared with JCM-1 (Fig. 5). The crystallinity and porosity of JCM-1(Cl⁻) were well retained after NH₃ adsorption, as confirmed by PXRD and N₂ adsorption data (Fig. 3). In the cycling experiment, JCM-1(Cl⁻) showed gradually decreasing NH₃ capacity after the first cycle (Fig. 4b and d), which means that the sample was not fully activated at room temperature. Activation of the sample after the 5th cycle at an elevated temperature of 358 K for 5 h regenerated JCM-1(Cl⁻) and the initial NH₃ uptake capacity of was almost recovered (Fig. 4d).

The isosteric heats (Qₛ) of adsorption for NH₃ within JCM-1 or JCM-1(Cl⁻) was calculated by employing the Virial method.⁴¹ Because of the hysteresis in the NH₃ adsorption isotherms, we calculated the Qₛ values using the desorption curves, which is also valid for explaining the change in the regeneration temperatures.⁴²–⁴⁴ The Qₛ values for NH₃ desorption in JCM-1(Cl⁻) were higher by ca. 20 kJ mol⁻¹ than JCM-1 in all coverages (inset in Fig. 5). The higher Qₛ value of JCM-1(Cl⁻) supports the reason for the increased regeneration temperature after ion substitution. The enhanced NH₃ affinity of JCM-1(Cl⁻) could be confirmed using density functional theory (DFT) calculations. For DFT calculations, the appropriate structural models of each framework were prepared using the crystal structures of JCM-1 and JCM-1(Cl⁻). The initial coordinate of NH₃ was loaded into each model structure, followed by further geometry optimization (see the ESIF). The NH₃ molecule showed stronger interaction with the imidazolium-Cl⁻ pair than the imidazolium-NO₃⁻ in the optimized structures, as the interaction enthalpies of JCM-1 and JCM-1(Cl⁻) with NH₃ molecule were calculated to be 20.8 kJ mol⁻¹ and 50.0 kJ mol⁻¹, respectively (Fig. S3 and S4†), which is qualitatively following the experimental observations.

Mechanism of ammonia adsorption on JCM-1 and JCM-1(Cl⁻)

A simple interpretation of the above observation is that the adsorbed NH₃ molecule interacts more strongly with Cl⁻ than NO₃⁻ ions. Contrary to this expectation, DFT calculations revealed a more delicate interplay between NH₃ and the imidazolium–anion pairs. Before NH₃ loading, NO₃⁻ or Cl⁻ is engaged in hydrogen bonding with the imidazolium in the framework. The distance between NO₃⁻ and imidazolium proton is 1.93 Å, whereas the distance between Cl⁻ and imidazolium proton is 2.21 Å (Fig. S5†). Upon adsorption, NH₃ molecules have to compete with the anions to form hydrogen bonding with the imidazolium proton. As expected, in the optimized structures of the NH₃-loaded JCM-1 and JCM-1(Cl⁻),
the distances between the anion and imidazolium proton increased (Fig. 5). On the other hand, a weak hydrogen bond between an NH$_3$ molecule and the imidazolium proton was detected. In the NH$_3$@JCM-1, the distance between the nitrogen atom of NH$_3$ and the imidazolium proton was 2.83 Å (Fig. 6a). Interestingly, in the NH$_3$@JCM-1(Cl$^-$), the distance was 2.51 Å, which is significantly shorter than that of JCM-1 and explains why JCM-1(Cl$^-$) exhibits the enhanced NH$_3$ affinity (Fig. 6b). As above mentioned, this interaction is similar to that for imidazolium-based ionic liquids having high ammonia solubility.\textsuperscript{35–38}

The interaction between NH$_3$ and the imidazolium group on the pore surface was experimentally observed by IR spectroscopy (Fig. S6†). We measured the IR spectra of the frameworks before and after exposure to NH$_3$ gas. In both structures, imidazolium C–H stretching bands\textsuperscript{45} (2900–3100 cm$^{-1}$) were slightly broadened and blue-shifted after exposure to the NH$_3$ atmosphere.\textsuperscript{46} The band-broadening and band-shift are indicative of the formation of the weak hydrogen bond between imidazolium and the NH$_3$ molecule, which is coincident with the DFT calculation results.

Dynamic breakthrough curves were obtained under dry and humid conditions (0% relative humidity (RH) and 80% RH) at a feed concentration of 1000 ppm NH$_3$ and a temperature of 298 K. We observed the increase in the adsorption amount of ammonia in JCM-1(Cl$^-$) in both humid and wet conditions, which shows the same tendency with the adsorption isotherms, while JCM-1 adsorbs only dry ammonia (Fig. S7–S10†).

Conclusions

In conclusion, we report JCM-1 which can adsorb a high amount of NH$_3$ at an ambient condition without structural deformation. JCM-1 is recyclable even at room temperature through the weak interaction between NH$_3$ and imidazolium functionalities by mimicking ionic liquids. Furthermore, we demonstrated the control of the NH$_3$ sorption property of JCM-1 by simple ion substitution in a post-synthetic manner. After exchanging the anion from nitrate to chloride, the affinity of MOF toward NH$_3$ was enhanced resulting in the increase in the uptake capacity while the regenerability was slightly decreased. This work suggests a new potential application of imidazolium-based MOFs for ammonia capture, as well as the effect of the anion species for ammonia adsorption in ionic porous materials.

Experimental

Materials and methods

All the reagents and solvents were commercially available and used as supplied without further purification. Elemental analysis (EA) for C, H, and N were carried out using Flash 2000 (Thermo Fisher Scientific Inc.). FT-IR measurements were processed in Bruker ALPHA FT-IR spectrometer. Single crystal X-ray diffraction (SXRD) analysis was carried out at synchrotron radiation of 2D-SMC and 6D-C&S UNIST-PAL (crystallography) at the Pohang Accelerator Laboratory (PAL, Korea). The powder XRD diffraction patterns were obtained on a Rigaku Smartlab system equipped with Cu sealed tube. Thermogravimetric analysis (TGA) were measured under N$_2$ atmosphere with a PerkinElmer Pyris. All gas sorption isotherms were measured with BELSORP-max volumetric adsorption equipment. Purified compounds were further dried under high vacuum (0.01–0.05 Torr).

MOF synthesis

JCM-1 ([Co(PzIm)(NO$_3$)$_2$], H$_2$PzIm = 1,3-bis(3,5-dimethyl-1H-pyrazol-4-yl)-1H-imidazol-3-ium) and JCM-1(Cl$^-$) ([Co(PzIm)(Cl)]$^-$) was synthesized following our previously reported methods.\textsuperscript{11}

Synthesis of JCM-1. Co(NO$_3$)$_2$·6H$_2$O (0.075 mmol, 21.9 mg) and H$_2$PzImCl (0.025 mmol, 7.3 mg) were dissolved in 0.5 mL of DMF in a 4 mL vial. The vial was stand in an oven at 120 °C for 3 days to yield plenty single crystals. The crystals were washed with water and DMF several times, followed by solvent exchange to methanol. Then, the crystals were activated under high vacuum at 393 K to afford JCM-1 ([Co(PzIm)(NO$_3$)$_2$]). Elemental analysis data: anal. calcd for (C$_{13}$H$_{15}$CoN$_7$O$_3$)(H$_2$O)$_2$: C, 35.54; H, 5.05; N, 22.32. Found: C, 35.31; H, 4.87; N, 22.32.

Synthesis of JCM-1(Cl$^-$). The as-synthesized JCM-1 powder was soaked in methanolic solution of 1 M LiCl. The solution was exchanged once a day for a week, followed by washing with fresh methanol to afford the product JCM-1(Cl$^-$). It is noteworthy that the exchange process was carried out longer (7 days) than before (3 days) for the full ion substitution. After anion exchange, the product was washed with fresh methanol several times and dried under high vacuum at 373 K. In addition to the previously reported FT-IR, PXRD and EDS analysis, the fully exchanged product was further confirmed by elemental analysis and single-crystal XRD analysis. Elemental analysis data of JCM-1(Cl$^-$): anal. calcd for (C$_{13}$H$_{15}$CoN$_6$Cl)(H$_2$O)$_{3.5}$: C, 40.48; H, 4.97; N, 21.79. Found: C, 40.15; H, 5.28; N, 21.61.

X-ray crystallographic analysis

Single crystal X-ray diffraction (SXRD) analysis was carried out at the synchrotron radiation of 2D-SMC at the Pohang Accelerator Laboratory (PAL, Korea). The SXRD patterns of crystals...
coated with paratone oil were collected at 100 K. Using Olex2, the structures were solved by ShelXT using Intrinsic Phasing. The crystal structure of JCM-1(Cl\textsuperscript{−}) was refined by ShelXL using least squares minimization. CCDC 1912377 contains the structural information for JCM-1(Cl\textsuperscript{−}).

Gas sorption experiments

Repeated NH\textsubscript{3} sorption using JCM-1. The activation/adsorption cycle was repeated over five times. Between each cycle, samples were activated at room temperature for 10 hours under dynamic vacuum. The NH\textsubscript{3} uptake patterns were well retained with negligible decrease in uptake capacity. The initial NH\textsubscript{3} adsorption capacity was fully restored after activating at a higher temperature.

Repeated NH\textsubscript{3} sorption using JCM-1(Cl\textsuperscript{−}). The activation/adsorption cycle of JCM-1(Cl\textsuperscript{−}) was repeated over five times. Between each cycle, samples were activated at room temperature under dynamic vacuum for 10 h. The NH\textsubscript{3} uptake capacity was decreased after the 1\textsuperscript{st} cycle, which means the NH\textsubscript{3} was not fully detached from the framework. Interestingly, in the rest of the cycle, the adsorption capacity was no longer significantly decreased. When regenerated at a higher temperature, the initial NH\textsubscript{3} adsorption capacity was recovered. It means that the capacity decrease in the cycle experiment was due to the enhanced affinity of the framework with NH\textsubscript{3} gas, not due to the collapse of the framework.

Isosteric heat of sorption

The isosteric heat of sorption \( Q_a \) was calculated using the virial type expression to fit the isotherms of 273 K and 298 K.

\[
\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i
\]

where \( P \) is the pressure of the gas phase at equilibrium (bar), \( N \) is the adsorbed amount per mass of adsorbent (mmol g\textsuperscript{−1}), \( T \) is the absolute temperature, \( a_i \) and \( b_i \) are virial coefficients, and \( m \) and \( n \) are numbers of coefficients used to describe the isotherms.

\[
Q_a = -R \sum_{i=0}^{m} a_i N^i
\]

Then, with the virial coefficient \( (a_i) \) and the following equation, the coverage-dependent isosteric heat of sorption was calculated. \( R \) is the universal gas constant.

DFT calculations

Both geometry optimizations and frequency calculations were performed using Gaussian 09 using B3LYP/6-31G(d,p) basis set.\textsuperscript{31} In the geometry optimization, the default tight convergence in the SCF cycle was used without any orbital symmetry constraints. For the calculation of MOFs, model structures were generated with appropriate pore structure based on crystallography data. Two-layer ONIOM method\textsuperscript{32} was used with B3LYP/6-31G(d,p) basis set for high level, and molecular mechanics using UFF force field\textsuperscript{33} for low level. Coordinates of the rigid cationic framework of MOF structures (JCM-1 and JCM-1(Cl\textsuperscript{−})) were fixed according to the crystallography data, while the geometry of anions (NO\textsubscript{3} \textsuperscript{−} or Cl\textsuperscript{−}) and ammonia molecule were optimized during the calculation. High level model systems in ONIOM calculation were selected as one imidazolium and its counter anions (NO\textsubscript{3} \textsuperscript{−} or Cl\textsuperscript{−}) with an ammonia molecule. The interaction enthalpies of the framework with the guest molecule were calculated from the difference in total energies for the model structure \( (H_{interaction} = H_{MOF} + H_{guest} - H_{MOF with guest}) \).

Breakthrough experiments

Breakthrough experiments were carried out with a BELCAT-II equipped with a BELMASS mass spectrometer. The pelletized sample was packed in the breakthrough column of 0.5 cm in width and 1.0 cm in height and activated at 120 °C for 10 h in a He flow. The dry ammonia breakthrough experiments were performed in 1000 ppm NH\textsubscript{3} gas balanced with He at 25 °C. In the case of wet ammonia breakthrough experiments, the sample was pre-saturated with humid (80% RH) He gas for 5 h at 25 °C prior to each measurement. And then, 1000 ppm NH\textsubscript{3} gas balanced with humid (80% RH) He was introduced to the sample-packed column for 18 h at 25 °C. The regeneration between consecutive ammonia breakthrough cycles was different to the degassing procedure. The sample was activated with 25 °C for 10 h in a He flow. The effluent gas signal was continuously monitored by the BELMASS mass spectrometer. The amount of adsorbed NH\textsubscript{3} was calculated by the integration of the breakthrough curve with ChemMaster program. The total gas flow was set at 30 scem in all cases.

In the case of dry ammonia breakthrough experiments, the amount of adsorbed ammonia in the breakthrough curve was calculated through the ChemMaster program by integrating the hatched area which is the gap between the elute curves of the saturated ammonia in the blank and the sample. The weight of glass beads in blank test (or the weight of the sample in breakthrough curve) was measured by comparing empty column weight and weight of column with beads (or sample) after activation. The calibration factor (count per mmol) of dry 1000 ppm breakthrough test was calculated with the ChemMaster program by choosing the flat region of blank test after NH\textsubscript{3} fully was eluted.

In the case of wet ammonia breakthrough experiments, the ammonia breakthrough curves after pre-humidification for 5 h were depicted. The amount of adsorbed ammonia in the breakthrough curve at 80% RH and 1000 ppm was calculated by the ChemMaster program by integrating the hatched area which is the gap between the elute curves of saturated ammonia in the blank and the sample. The weight of glass beads in blank test (or the weight of the sample in the breakthrough) was measured by comparing empty column weight and weight of column with beads (or sample) after activation. The calibration factor (count per mmol) of the breakthrough test at 80% RH and 1000 ppm was calculated by choosing the flat region of the blank test after NH\textsubscript{3} was fully eluted. It should be noted that the ammonia breakthrough curve at dry 1000 ppm and that at 80% RH and 1000 ppm were not compatible in retention time.
because two have distinct blank breakthrough curves and so the calibration factors.

Conflicts of interest

There are no conflicts of interest to declare.

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