High capacity ammonia adsorption in a robust metal–organic framework mediated by reversible host–guest interactions†

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To understand the exceptional adsorption of ammonia (NH₃) in MFM-300(Sc) (19.5 mmol g⁻¹ at 273 K and 1 bar without hysteresis), we report a systematic investigation of the mechanism of adsorption by a combination of in situ neutron powder diffraction, inelastic neutron scattering, synchrotron infrared microspectroscopy, and solid-state ⁴⁵Sc NMR spectroscopy. These complementary techniques reveal the formation of reversible host–guest supramolecular interactions, which explains directly the observed excellent reversibility of this material over 90 adsorption–desorption cycles.

Annual global production of ammonia (NH₃) is around 170 million tonnes reflecting its role as a major feedstock for agriculture and industry.¹ The high hydrogen content (17.8 wt %) and hydrogen volume density (105 kg m⁻³) of NH₃ make it a desirable carbon-free hydrogen carrier, and NH₃ is therefore regarded as a surrogate for the H₂ economy. However, the corrosive and toxic nature of NH₃ makes it a target gas to be tailored by grafting the pore interior with functional groups to anchor the gas through coordination, hydrogen bonding, electrostatic interactions, acid–base interactions or π–π stacking.²–⁷ A large number of MOFs with functional groups (e.g. –COOH,² –OH⁸) and open metal sites⁹ have been reported to impart enhanced affinity to gas molecules. Several state-of-the-art MOFs, such as MOF-177,¹⁰ MₓCl₂BBTA {BBTA = 1H,5H-benzo[1,2-d:4,5-dʹ]bistriazolate; M = Co, Mn},¹¹ M₂Cl₂(BTDD) {BTDD = bis[1H-1,2,3-triazolo[4,5-b][4,5-c’-i] dibenzo[1,4]dioxin; M = Mn, Co, Ni and Cu}¹² as well as MFM-300(M) (M = Al, Fe, V, Cr, In),⁶¹⁴ have been investigated for NH₃ adsorption. However, due to the reactive and corrosive nature of NH₃, many MOF systems showed structural degradation and/or significant loss of uptake after consecutive cycles owing to irreversible host–guest binding. So far, only a very limited number of MOFs exhibit reversible NH₃ sorption over multiple cycles.⁵,⁶,¹³–¹⁶ Unravelling the molecular details of host–guest interactions is of critical importance if new efficient NH₃ storage systems are to be developed. This is however highly challenging, not least because hydrogen atoms are invisible in X-ray diffraction experiments and NH₃ molecules can act as a rapid rotor in solid state. The mechanism of adsorption of NH₃ in MFM-300(Sc) was examined systematically using gas isotherms, breakthrough experiments, in situ solid-state nuclear magnetic resonance (ssNMR) spectroscopy, synchrotron infrared microspectroscopy, neutron powder diffraction (NPD) and inelastic neutron scattering (INS) techniques, coupled with DFT modelling. Distinct new insights have been gained into the mechanism of adsorption compared with a recent report based on theoretical and infrared spectroscopic studies of this system.¹⁷ Importantly, we found the exceptional NH₃ uptake (19.5 mmol g⁻¹ at 273 K and 1 bar) by MFM-300(Sc) was mediated by reversible host–guest and guest–guest hydrogen bond interactions. The moderate strength of the host–guest interaction in MFM-300(Sc) leads to excellent adsorption reversibility and stability with full retention of the capacity over 90 cycles.

MFM-300(Sc) shows a three-dimensional framework containing [ScO₄(OH)₂] octahedra which are connected via the...
cis-$\mu_2$-OH groups to infinite chains, and further coordinated by the BPTC$^{1-}$ ligand (H$_4$BPTC = biphenyl-3,3,5,5-tetracarboxylic acid) (Fig. S1, ESI†). Desolvated MFM-300(Sc) shows a Brunauer–Emmett–Teller (BET) surface area of 1390 m$^2$ g$^{-1}$ and a pore volume of 0.48 cm$^3$ g$^{-1}$ (Fig. S2, ESI†). MFM-300(Sc) exhibits high thermal stability up to 500 °C under N$_2$ (Fig. S3, ESI†) and high chemical stability in aqueous solutions of pH of 7–12 as well as in various organic solvents (Fig. S4, ESI†).

Adsorption isotherms of NH$_3$ for MFM-300(Sc) were measured at 273–313 K, where an exceptional uptake of 19.5 mmol g$^{-1}$ was recorded at 273 K and 1.0 bar (Fig. 1a), reducing to 13.5 mmol g$^{-1}$ at 298 K. MFM-300(Sc) shows the highest NH$_3$ uptake among the MFM-300(M) family$^{6,14}$ primarily due to its large pore size and pore volume allowing the accommodation of additional NH$_3$ molecules in the pore. MFM-300(Sc) shows an NH$_3$ uptake of 13.5 mmol g$^{-1}$ at 298 K and 1.0 bar, comparing favourably with state-of-the-art materials (Fig. 1d and Table S6, ESI†). The uptake of NH$_3$ in MFM-300(Sc) between 273 and 313 K decreases gradually with increasing temperature, consistent with an exothermic adsorption mechanism.$^{19}$ The isosteric heat of adsorption ($Q_a$) for NH$_3$ in MFM-300(Sc) decreases from 60 to 30 kJ mol$^{-1}$ with increasing loading of NH$_3$ from 1 to 10 mmol g$^{-1}$ (Fig. S7, ESI†), confirming the presence of moderate adsorbate–adsorbent binding interaction. The repeated isotherm of NH$_3$ at 273 K using powder X-ray diffraction (PXRD) (Fig. S5, ESI†). The ability of MFM-300(Sc) to capture NH$_3$ at low concentrations (1000 ppm) was confirmed by dynamic breakthrough experiments at 298 K with a dynamic uptake of 1.65 mmol g$^{-1}$, consistent with that measured by isotherms (1.74 mmol g$^{-1}$ at 10 mbar, equivalent to 1000 ppm; Fig. 1c). With an exceptional adsorption capacity and excellent regenerability, MFM-300(Sc) represents a promising candidate for applications in NH$_3$ storage and transport.

In situ NPD data of MFM-300(Sc) as a function of ND$_3$ loading were collected and Rietveld refinements revealed the preferential binding sites for ND$_3$ (Fig. 2). Interestingly, the NH$_3$-induced rearrangement of metal–ligand (Sc–O) bonds via insertion of NH$_3$ molecules into the MOF upon ND$_3$ binding as predicted by a DFT study$^{17}$ was not observed here. For MFM-300(Sc)–(ND$_3$)$_{1.25}$, {[Sc$_2$(L)(OD$_{0.75}$H$_{0.25}$)$_2$]$(ND_2.42$H$_{0.38}$)$_{2.6}$}, two distinct binding sites were identified (Fig. 2c and d). Site I is fully occupied by ND$_3$ molecules (1 ND$_3$/Sc), with hydrogen bonding between the ND$_3$-OH groups and the ND$_3$ molecule $[\text{O}_{\text{bridge}} - \text{H} \cdot \cdot \cdot \text{ND}_3 = 1.96(1) \text{ Å}]$ (Fig. 2a and b). At the higher loading of MFM-300(Sc)–(ND$_3$)$_{2.6}$, {[Sc$_2$(L)(OD$_{0.75}$H$_{0.25}$)$_2$]$(ND_2.42$H$_{0.38}$)$_{2.6}$}, only one binding site was found, interacting primarily with the bridging $\mu_2$-OH groups at the four corners of its square-shaped channel $[\text{O}_{\text{bridge}} - \cdot \cdot \cdot \text{ND}_3 = 1.93(1) \text{ Å}]$. This is complemented by additional electrostatic interactions $[\text{ND}_3 \cdot \cdot \cdot \text{aromatic rings} = 3.13(1) \text{ Å}]$, and hydrogen bonding $[\text{ND}_3 \cdot \cdot \cdot \text{O}_{\text{ligand}} = 3.24(1) \text{ Å}]$. Site II (0.3 ND$_3$/Sc) exhibited hydrogen bonding with the ND$_3$ at site I $[\text{O}_{\text{bridge}} - \cdot \cdot \cdot \text{ND}_3 = 3.07(1) \text{ Å}]$, propagating along the 1D channel to form a cooperative $[\text{ND}_3]_{\infty}$ network. Similar to other MFM-300 analogues,$^{6,14}$ hydrogen/deuterium site exchange was also observed between the adsorbed ND$_3$ molecules and the $\mu_2$-OH group for MFM-300(Sc).
The analysis of the NPD data were entirely consistent with information from solid-state NMR spectroscopy. Upon loading MFM-300(Sc) with NH$_3$, only slight structural modifications were observed, and the crystalline nature of the framework was retained. $^{45}$Sc magic angle spinning (MAS) NMR spectroscopy confirmed that the geometry around the Sc(III) centre was not notably distorted by interaction with NH$_3$, with the $\mu_2$-OH groups (Fig. S11a, ESI†) and $\{^1$H$\}^{13}$C CPMAS NMR spectra showing that the carboxyl resonance from the linker is unaffected upon NH$_3$ loading (i.e. minimal metal site distortion). However, the resonances assigned to the aromatic carbons do show that the carboxyl resonance from the linker is unaffected upon NH$_3$ loading (i.e. minimal metal site distortion). However, the resonances assigned to the aromatic carbons do shift, reflecting an interaction of the rings with the guest molecules (Fig. S11b, ESI†). The interaction of NH$_3$ with the MOF was also investigated using 2D $^1$H-$^{45}$Sc dipolar correlation (HETCOR) NMR spectroscopy (Fig. 3). The spectrum of pristine MFM-300(Sc) (Fig. 3a) shows clear cross peaks between aromatic protons (from the linker), as well as from hydroxyl protons ($\mu_2$-OH groups), with the Sc(III) site, demonstrating a close proximity between these atomic environments. The corresponding spectrum of NH$_3$-loaded MFM-300(Sc) is substantially different. Whilst cross peaks with aromatic protons unchanged, cross peaks with $\mu_2$-OH groups have moved to higher chemical shifts, indicating the presence of hydrogen-bonding, and a new weak cross peak is observed and assigned to pore-confined NH$_3$ protons. In situ synchrotron FTIR microspectra were recorded at 298 K (Fig. 3e and f). The characteristic O–H stretching mode of the $\mu_2$-OH group is observed at 3678 cm$^{-1}$, which reduces in intensity and broadens upon loading of NH$_3$. The band at 3404 cm$^{-1}$ is assigned to the N–H stretching of NH$_3$, and this exhibits a red shift to 3390 cm$^{-1}$.$^5$,$^14$ The bands at 1614 and 1440 cm$^{-1}$, assigned to $\nu_\text{as}$(COO$^-$) and $\nu_\text{s}$(COO$^-$), respectively,$^26$ show small red shifts upon adsorption of NH$_3$ ($\Delta = 4 - 7$ cm$^{-1}$), consistent with interaction between NH$_3$ and carboxylate groups. The bands between 3800 and 1400 cm$^{-1}$ for the local framework remain unchanged upon re-activation, confirming the high structural stability of MFM-300(Sc). Thus, the ssNMR and FTIR studies verify that NH$_3$ is hydrogen-bonded to the $\mu_2$-OH groups via the lone pair of electrons on nitrogen, fully consistent with the NPD analysis.

INS spectra of bare and NH$_3$-loaded MFM-300(Sc) were also collected (Fig. S12, ESI†) and simulated using DFT calculations based upon the structural models derived from NPD analyses (Fig. S13, ESI†). The difference spectra (Fig. 4a), which were obtained by subtracting the spectrum of the bare MOF from that of the NH$_3$-loaded MOF, show the vibrational features of both the adsorbed NH$_3$ molecules and the changes for the MOF host. The peaks in the low energy region (Fig. 4b) are primarily due to the vibrational modes of adsorbed NH$_3$ molecules, with a small contribution due to changes in the lattice modes of the framework. The agreement between experimental and simulated spectra in terms of the overall profile allows unambiguous assignment of all major peaks. Specifically, the bands between 45 and 116 cm$^{-1}$ are assigned to the translational motion of the NH$_3$, which includes the vibration of NH$_3$ molecules perpendicular to and along the molecular C$_2$ axis and the hybrid of these modes. Peaks at 132 and 172 cm$^{-1}$ are due to rotational motion of the NH$_3$ around its C$_3$ axis. Bands between 207 and 334 cm$^{-1}$ are assigned to the rocking modes of the NH$_3$. Compared to the spectrum of NH$_3$ in the solid state, where each NH$_3$ forms a 3D hydrogen bonding network with 6 adjacent NH$_3$ molecules, bands in all regions for the adsorbed NH$_3$ shift to lower energy and exhibit more broad features, indicating more dynamic environment for the adsorbed NH$_3$. The features in the higher energy region mainly reflect the modes of the framework (Fig. 4c). Features I and III are due to the broadening of the peaks at 692 and 934 cm$^{-1}$ for bare MFM-300(Sc), and are assigned to the C–H rocking out of the C$_6$ plane, in-phase and anti-phase, respectively. Feature VI at higher frequency between 1090 and 1163 cm$^{-1}$ shows reduced intensity upon adsorption of NH$_3$, and is assigned to the H$_{\text{ring}}$ rocking within the C$_6$ plane. Features II and IV originate from a significant blue shift of the peak at 754 cm$^{-1}$ in the spectrum of bare MFM-300(Sc) to 987 cm$^{-1}$ in the spectrum of NH$_3$-loaded MFM-300(Sc). This is assigned to the rocking of $\mu_2$-OH within the Sc–O–Sc plane. Interestingly, the features involving the motions of H$_{\text{ring}}$ show only broadening and a decrease in intensities, while the features involving the motion of the $\mu_2$-OH experience changes in energy. This indicates a stronger interaction between NH$_3$ and the $\mu_2$-OH than with H$_{\text{ring}}$ centres. Feature V in the difference spectrum is due to the umbrella motion of adsorbed NH$_3$. Thus, the combined INS and DFT study has visualised directly the host–guest binding dynamics.
consistent with the reversible and high adsorption of NH₃ in MFM-300(Sc).

In summary, MFM-300(Sc) comprised of metal-oxide chains with bridging –OH groups shows exceptional adsorption capacity (19.5 mmol g⁻¹ at 273 K and 1 bar) and regenerability for NH₃. In situ NPD analysis, ⁴５Sc ssNMR spectroscopy, synchrotron FTIR and INS/DFT studies have unambiguously visualised the binding interactions and dynamics of NH₃ within the pores of MFM-300(Sc). This in-depth understanding of the structure–function relationship with these host-guest systems will enable the rational design of potential materials with desired properties.

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Conflicts of interest
The authors declare no competing interest.

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