Sulfonated and Ordered Mesoporous Polymers for Reversible Adsorption of Ammonia: Elucidation of Sequential Pore-Space Diffusion

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Abstract

NH₃ adsorption and separation are pivotal for its safety and efficient utilization, but most solid adsorbents show either low capacity or unsatisfied separation performance. Herein, we report sulfonated and ordered mesoporous polymers (SOMPs) synthesized from solvent-free manual-grinding of resorcinol and 1,4-phthalaldehyde with copolymer template, curing at 140~220°C, simultaneous sulfonation and template removal by treating with H₂SO₄. The prepared SOMPs possess ordered mesopores with abundant microporosity, large surface areas (~697 m²/g), and extremely-high –SO₃H densities (~4.48 mmol/g). Their NH₃ capacities are as high as 15.09 mmol/g (25°C, 1.0 bar), exhibiting NH₃ breakthrough time and saturated capacity up to 138 min/g and 6.16 mmol/g, respectively (5.0v%NH₃/23.75v%N₂/71.25v%H₂). Versatile characterizations together with molecular dynamics simulations demonstrate the superior NH₃ adsorption performance originates from strong affinity of –SO₃H group with NH₃ in sequential pore-space of SOMPs, which not only enhances the molecular recognition ability, but also effectively promotes NH₃ fast diffusion inside SOMPs.

Introduction

Ammonia (NH₃) has constituted the basement for the development of modern agriculture, since it is the essential feedstock for synthesizing various nitrogen fertilizers.^{1,2} NH₃ is also proposed as the safe medium for storage and transportation of H₂ due to its large hydrogen density (11.8 wt.%) and relatively easy liquidation (b.p. –33.5 °C).³ The throughput of NH₃ has reached as high as ~200 million tons per year across the world.⁴ However, the effective separation and purification of NH₃ from the NH₃ synthesis process is still a challenge, and imposes significant energy consumption on the whole process. On the other hand, the utilization of NH₃ inevitably leaves a trace of NH₃ in the tail gas of industrial process, which will cause severely environmental issues and significant threats to human health.⁵ Therefore, effective separation and recycling of NH₃ is highly demanded during its synthesis and application in the industry.

To tackle mentioned problems, many materials have been engineered for the selective and reversible capture of NH₃. For example, ionic liquids (ILs)^{6–10} and deep eutectic solvents (DESs)^{11–15} with extremely low volatility and tunable properties were investigated for NH₃ absorption. However, the liquid absorption requires continuous transportation of liquid absorbents in the pipelines and towers during the gas absorption process, and the high viscosity of ILs and DESs interferes their practical applications. Alternatively, zeolites,¹⁶ activated carbons,¹⁷ metal-organic frameworks (MOFs),^{5,18} and porous organic polymers (POPs)¹⁹ with permanent nanoporosity and tailorable frameworks are promising candidates for NH₃ adsorption. These solid adsorbents are normally fixed into two parallel towers, and operated successively for adsorption and desorption, thus avoiding the transportation issues associated with liquid absorbents. In addition, the solid adsorption features low energy consumption, free from corrosion, and low investment for the facilities in relative to the liquid absorption.

Regarding the solid adsorption for selective and reversible capture of NH_3 , previous works mainly focused on construction of abundant micropores with tunable diameter to improve the physical adsorption of NH_3 ,^{20,21} and incorporation of active sites with proper affinity to improve the chemical adsorption of NH_3 .^{22,23} Although micropores are favorable for the condensation of NH_3 due to the capillary effect, the filling capacity of micropores are limited by their low volumes. To date, there are scarce studies noting the importance of mesopores with enhanced pore volumes in the selective adsorption of NH_3 . Particularly, the mesopores with uniform size and long-range orderings can provide not only enlarged space for NH_3 filling, but also the barrier-eliminated channels for NH_3 diffusion.

The active sites for the chemical adsorption of NH_3 mainly include open metal centers^{23–25} and acidic groups.^{26,27} The former ones enable multiple coordination interaction with NH_3 , and the latter ones enhance acid-base interaction with NH_3 . However, the incorporation of these active sites normally suffers from complicated routes, constrained grafting degree, harsh conditions and/or expensive reagents.^{28–31} It will be very fascinating if the functional materials for NH_3 reversible capture can be synthesized through a sustainable and cost-effective route.

Herein, we report a successful synthesis of highly sulfonated and ordered mesoporous polymers (SOMPs) through a solvent-free self-assembly route. As illustrated in Scheme 1, resorcinol and 1,4-phthalaldehyde monomers together with triblock copolymer template were mixed thoroughly by manual grinding at room temperature, followed by curing at 140~220 °C to result in pristine ordered hexagonal mesoporous polymers (OMPs),^{32,33} which were then treated with concentrated H_2SO_4 to simultaneously realize high-degree sulfonation and template removal (see Experimental Section for the detailed synthetic procedures). It was found that the synthesized SOMPs enable remarkable adsorption of NH_3 , with the capacities of 11.53~15.09 mmol/g for pure NH_3 at 25 °C and 1 bar, and as high as 6.16 mmol/g for 5 vol.% of NH_3 at 25 °C. The adsorption of NH_3 on the SOMPs is also highly selective to those of N_2 and H_2 , and totally reversible without loss of NH_3 capacities after 30th recycling. With the assistance of multiple characterizations and molecular dynamics simulations, it is revealed that the NH_3 molecules prefer to be adsorbed in micropores at low loadings, and then in mesopores at medium to high loadings. This is for the first time that the sequential pore-space diffusion of NH_3 , and the importance of mesopores in the selective adsorption of NH_3 were systematically elucidated.

Results And Discussion

The synthesized SOMPs were denoted as OMP- SO_3H - x , where x stands for curing temperature. The porous structure of the synthesized SOMPs was characterized by XRD, N_2 sorption and electron microscopy, as given in Figure 1. Figure 1a shows small-angle XRD patterns of various SOMPs, which display three well-resolved diffraction peaks at around 0.88°, 1.52° and 1.76°. These peaks can be indexed to (100), (110) and (200) reflections, suggesting the formation of ordered mesostructure with two-dimensional (2-D) hexagonal symmetry ($p6mm$) in these samples. However, wide-angle XRD patterns

of the SOMP_s display only two weak peaks at 17.8° and 42.5° (see Figure S1), suggesting their non-crystalline networks. Figure 1b shows N₂ adsorption-desorption isotherms at -196°C of the SOMP_s, which display type IV profiles with H1 hysteresis loops. Such N₂ sorption isotherms indicate the presence of ordered hexagonal mesopores with abundant micropores in the SOMP_s. The ordered hexagonal mesopores are undoubtedly formed by the oriented assembly of polymer precursors with F127 micelles.^{34,35} The micropores are originated from the embedding of some F127 chains in the mesopore walls,^{36,37} and the removal of which leaves the voids with sub-nanometer size. Figure 1c shows pore size distributions of the SOMP_s, which display trimodal profiles with the pore size of 0.63~0.73, 1.17~1.35 and 6.34~13.60 nm. The textural parameters of the SOMP_s calculated from the N₂ adsorption data are summarized in Table 1. It can be seen that the surface areas, micropore volumes and total pore volumes of the SOMP_s firstly increase but then decrease with the increase of curing temperatures. Thus, the OMP-SO₃H-180 exhibits the highest porosity among the SOMP_s. However, the pore size of the SOMP_s gradually increase with curing temperatures. Thus, the OMP-SO₃H-220 exhibits the largest pore size among these SOMP_s.

Table 1

Textural parameters and sulfur contents of the SOMP_s.

SOMP	S _{BET} ^{a)}	V _m ^{b)}	V _t ^{c)}	D _p ^{d)}	Sulfur content ^{e)}
	(m ² /g)	(cm ³ /g)	(cm ³ /g)	(nm)	(wt.%)
OMP-SO ₃ H-140	545	0.12	0.44	0.73, 1.26, 6.34	14.36
OMP-SO ₃ H-160	620	0.13	0.77	0.73, 1.34, 8.69	11.41
OMP-SO ₃ H-180	697	0.15	0.85	0.68, 1.35, 8.63	12.97
OMP-SO ₃ H-200	614	0.14	0.66	0.73, 1.28, 13.12	9.38
OMP-SO ₃ H-220	428	0.09	0.63	0.63, 1.17, 13.60	8.96

a)

Surface area calculated by BET equation;

b)

micropore volume calculated by DFT method;

c)

total pore volume calculated by DFT method;

d)

pore size extrapolated from pore size distribution;

e)

sulfur content determined by elemental analysis.

Figure 1d and Figure S2 show SEM images of the OMP-SO₃H-180, exhibiting ample cavities with well-ordered features, which are similar to those in other SOMP_s (Figures S3~S4). Meanwhile, TEM images of the sample show highly ordered mesopores viewed from (110) direction associated with 2-D hexagonal symmetry (*p6mm*) and open cylinder shape can be clearly observed in the OMP-SO₃H-180 (Figure 1e). In addition to the ordered mesopores, starry worm-like holes with sub-nanometer size can be clearly observed in the sample, suggesting they were also rich in microporosity. Figures 1f~i show STEM image with elemental mapping of the OMP-SO₃H-180. It can be seen that C, O and S atoms are uniformly

distributed in the SOMP. The S atoms are originated from the grafted $-\text{SO}_3\text{H}$ group in the SOMP. According to the elemental analysis, the sulfur contents of the SOMP are 8.96~14.36 wt.% (Table 1 and S1), corresponding to $-\text{SO}_3\text{H}$ densities of 2.80~4.48 mmol/g. Such concentration of the $-\text{SO}_3\text{H}$ group supports the enhanced sulfonation degree of the SOMP, much higher than those of the sulfonated materials reported yet. It is also noted that the sulfur contents of the SOMP decrease with the increase of curing temperatures. This might be a result of the more rigid structure of the SOMP as the curing temperatures increase, so that the $-\text{SO}_3\text{H}$ group became more difficult to be grafted onto the frameworks. Meanwhile, the H^+ capacity of the SOMP were up to 4.4 mmol/g, which is a record value among the sulfonated porous solid acids yet.

The chemical structures of the SOMP were characterized by solid-state NMR, XPS spectra, as shown in Figure 2. In comparison with non-sulfonated OMP, the FT-IR spectra of SOMP displayed additional four characteristic peaks at around 1016, 1040, 1125 and 1171 cm^{-1} , which are ascribed to the signals of $-\text{SO}_3\text{H}$ groups^{38,39} (Figure S5 and Figure S6). Figure 2a shows ^{13}C solid-state NMR spectra of the SOMP, displaying a series of peaks associated with the carbon atoms in different environments, which include the $-\text{CH}_2-$ bridges between benzene rings (20.1 and 40.1 ppm), aromatic carbon atoms without being attached by heteroatoms (128 ppm), aromatic carbon atoms attached by $-\text{OH}$ and $-\text{O}-\text{SO}_3\text{H}$ groups (150 and 141 ppm), and terminal $-\text{CH}_3$ and $-\text{CHO}$ groups attached to benzene rings.²⁸ To study the intrinsic acidity of the SOMP, reliable and classical ^{31}P solid-state NMR combining TMPO probe molecule were carried out (see Figure 2b). It can be seen a pronounced and symmetric peak at ~79 ppm, which were ascribed to TMPO adsorbed on the strong acidic $-\text{SO}_3\text{H}$ site with uniform distribution.⁴⁴ High acid density combined with strong and uniform acid strength play crucial roles for their applications in selective capture of alkaline gas such as NH_3 . Figures 2c~d, Figure S7 and Figure S8 show XPS spectra of the SOMP. The $\text{C}1\text{s}$ spectra can be deconvoluted into three peaks at 284.4, 285.3 and 286.1 eV, ascribing to $\text{C}-\text{C}/\text{C}-\text{H}$ bonds, $\text{C}-\text{S}$ bond and $\text{C}-\text{O}$ bond respectively.^{40,41} The $\text{O}1\text{s}$ spectra can be deconvoluted into two peaks at 531.4 and 532.9 eV, ascribing to $\text{O}-\text{S}$ bond and $\text{O}-\text{C}/\text{O}-\text{H}$ bonds.⁴² The $\text{S}2\text{p}$ spectra can be deconvoluted into two peaks at 166.5 and 167.8 eV, ascribing to $\text{S}-\text{C}$ bond and $\text{S}-\text{O}$ bond.^{26,43} All these results confirm successful grafting of $-\text{SO}_3\text{H}$ group onto OMPs' framework.

As a result, given the high acid density with suitable acid strength, artistic microporosity tandem ordered mesoporosity, the SOMP are expected to have great potential application in the separation of NH_3 . The performance of the SOMP for NH_3 selective adsorption was firstly examined, as depicted in Figure 3. Figures 3a~b show the NH_3 sorption isotherms of the SOMP at 25 and 50°C, which give obviously non-ideal profiles, indicating the strong interaction of the SOMP with NH_3 . However, the NH_3 adsorption isotherm of non-sulfonated sample OMP-180 exhibits an almost ideal profile, with much lower NH_3 capacities than those of the other SOMP (see Figure S9). Therefore, the strong interaction of SOMP with NH_3 is originated from the acid-base affinity between grafted $-\text{SO}_3\text{H}$ and NH_3 molecules, while $-\text{OH}$ group with weak acidity in the SOMP play relatively low role for the adsorption of NH_3 . It is noted that

NH₃ capacities of the SOMP_s firstly increase but then decrease with curing temperatures. Thus, the OMP-SO₃H-180 exhibits the highest NH₃ capacities among the SOMP_s. This is well consistent with the variation of porosity for the SOMP_s with curing temperatures. Additionally, the NH₃ capacities of the SOMP_s decrease with the increase of temperatures, suggesting the exothermic nature of NH₃ adsorption process. The isosteric heats of NH₃ adsorption by OMP-SO₃H-180 and OMP-SO₃H-200 were calculated by the Clausius-Clapeyron equation, distributing in the range of -65 ~ -45 kJ/mol (Figure S10).^{12,19} The magnitude of NH₃ adsorption heats agree well with the non-ideal adsorption of NH₃ by the SOMP_s. Overall, the NH₃ capacities of the SOMP_s are very high, with the value of 15.09 mmol/g for the OMP-SO₃H-180 at 25°C and 1 bar, which is quite competitive in relative to those of other solid adsorbents reported in the literature (Table S2). Owing to the non-ideal adsorption of NH₃ by SOMP_s, the NH₃ capacities of them at low pressures are even more significant. For example, the OMP-SO₃H-180 can adsorb 6.6 mmol/g of NH₃ at 25°C and 0.05 bar, being superior to most other solid adsorbents reported in the literature (Table S2). This result is particularly important, because the contents of NH₃ in industrial gas are normally low, and the performance of solid adsorbents for adsorption of NH₃ at low pressures is more concerned.^{45,46}

For the separation of NH₃, the most important task is to selectively adsorb NH₃ from N₂ and H₂ mixture. Previous works have illustrated that the adsorption of inert gases on mesopore walls is much weaker than that on micropore walls due to the reduced capillary condensation effect.^{28,47} However, the adsorption of acidic gases over mesoporous adsorbents can be well maintained by grafting basic sites onto the mesopore walls. Thus, highly efficient and selective adsorption of acidic gases from inert gases can be realized by constructing abundant mesopores and grafting suitable basic sites in solid adsorbents. It is deduced that similar principles can also be applied for selective separation of NH₃ from N₂ and H₂. Since the SOMP_s have abundant mesopores and micropores as well as high -SO₃H density, it is anticipated that the adsorption of inert gases N₂ and H₂ by them is much lower than that of basic gas NH₃. As expected, the N₂ and H₂ adsorption isotherms of the SOMP_s at 25°C (Figure S11~S12) display almost ideal profiles with the N₂ and H₂ capacities being about two magnitudes lower than the NH₃ capacities. Figures 3c~d shows the selectivities of the SOMP_s for NH₃/N₂ and NH₃/H₂ at 25°C and 1 bar, obtaining from ideal adsorption solution theory.^{48,49} It can be seen that when the molar fraction of NH₃ in gas phase is 0.05, the IAST selectivities of NH₃/N₂ and NH₃/H₂ for the OMP-SO₃H-180 reach 453 and 1768. Figures 3e~f show the breakthrough curves for NH₃/N₂/H₂ mixed gas over the OMP-SO₃H-180 at 25 and 50°C. It can be seen that N₂ and H₂ instantly penetrate the fixed bed, indicating negligible adsorption of the two gases. Interestingly, the penetration of NH₃ starts at ~138 min/g and completes at ~263 min/g at 25°C. Similarly, the penetration of NH₃ still starts at ~124 min/g and completes at ~255 min/g at 50°C. The accelerated penetration of NH₃ is ascribed to the decreased NH₃ capacities as the temperatures increase. By integrating the breakthrough curves, it is estimated that the OMP-SO₃H-180 can adsorb 6.16 and 5.53 mmol/g of NH₃ from NH₃/N₂/H₂ (5/23.75/71.25 vol.) mixture at 25 and 50°C,

respectively. The values agree well with the NH_3 capacities at 0.05 bar calculated from the NH_3 isotherms (6.28 and 5.03 mmol/g). More importantly, the above penetrated parameters of OMP- SO_3H -180 are very well maintained even after being treated saturated water vapor at 50°C for 2 h, suggesting the excellent water resistance of SOMP for NH_3 adsorption (Figure S13). These results confirm that the SOMP can be used as highly efficient and selective adsorbents for NH_3 from N_2 and H_2 , much better than variously reported adsorbents in the field.^{26,50,51}

The adsorption/desorption behavior of NH_3 on the SOMP was then examined, as shown in Figure 4. Figure 4a shows recycling of the OMP- SO_3H -180 for NH_3 adsorption at 25°C and 1.0 bar, while desorption was performed at 150°C and 0.001 bar. Noting that the SOMPs are stable enough at such desorption temperature (Figure S14). It can be seen that the NH_3 capacity of the OMP- SO_3H -180 remains almost unchanged after 30th cycling, giving the attenuation ratio only 1.6%. In contrast, the attenuation ratio on NH_3 capacity over MOFs adsorbents (e.g. Ce-MOF) was as high as 39.1% under identical condition (Figure S15). Therefore, the adsorption of NH_3 on the SOMP is totally reversible and quite durable. Figure 4b shows *in-situ* DRIFTS spectra of the OMP- SO_3H -180 with 0.05 vol.% of NH_3 purge at 25°C. As exposure time prolongs, four characteristic peaks associated with chemically adsorbed NH_3 gradually appear with increased intensities. For instance, the characteristic bands (1720, 1539, and 1265 cm^{-1}) correspond to the asymmetric, and symmetric bending vibrations of NH_4^+ , and the band at 1450 cm^{-1} is assigned to NH_3 interacts with $-\text{SO}_3\text{H}$ group.^{52,53} Figure 4c shows NH_3 -TPD MS curve of the OMP- SO_3H -180, exhibiting two NH_3 desorption peaks centered at around 113°C and 188°C. Considering the uniform acid strength of the sample determined by ^{31}P solid-state NMR spectra, two desorption peaks should be resulted from the $-\text{SO}_3\text{H}$ located in different microenvironment of micropores and ordered mesopores. Similar phenomenon can also be confirmed by controlling NH_3 adsorption behavior, as given in Figure 4d. Notably, the fresh OMP- SO_3H -180 has two adsorption steps distributed at 0~0.1 bar and 0.1~1.0 bar, which show quadratic function and linear function characteristics respectively. The former was resulted from NH_3 interacts with $-\text{SO}_3\text{H}$ in micropores due to capillary condensation effect, the latter was resulted from NH_3 interacts with $-\text{SO}_3\text{H}$ in mesopores. After saturated adsorption, controllable desorption of NH_3 in mesopores was performed by treating the sample at suitable temperature (see experimental section for the mesoporous adsorption measurements). The NH_3 isotherm of the degassed sample shows only linear function characteristic, which is consistent with the NH_3 isotherm in mesoporous adsorption part of the fresh OMP- SO_3H -180. The result confirms novel sequential pore-space diffusion rule of NH_3 in interconnected micropores and ordered mesopores, the diagrammatic sketch was depicted in Figure S16. As a result, the SOMP shows a record integrated performance in selective adsorption and separation of NH_3 , far better than the industrial H-ZSM-5 zeolite with pure micropores and sulfonated mesopores silica of SBA-15- SO_3H (Figure S17, and Table S3).

Based on the above statement, the sequential pore-space diffusion in interconnected micropores and ordered mesopores plays a key role for their excellent integrated performance in NH_3 selective capture

and separation. To better understand the inherent diffusion rule of NH_3 , molecular dynamics simulations were performed as a complement to the experimental approaches, which can reflect the adsorption and diffusion dynamical process of NH_3 in the SOMP s on theoretical level. Figure S18 shows the simulated frameworks of the OMP-SO₃H-160 and OMP-SO₃H-180 possess both microporous and mesoporous channels. The two best SOMP s with excellent NH_3 adsorption performance. Noting that OMP-SO₃H-180 owns more micropores while OMP-SO₃H-160 owns more mesopores because of their density difference. Then the adsorption and diffusion of NH_3 molecules in the two SOMP s were studied. Figure 5 shows the snapshot of NH_3 molecules adsorption and diffusion trajectory of one representative NH_3 molecule in the OMP-SO₃H-180 at low, medium and high loadings. At low loading, due to the strong acid-base interaction between -SO₃H group and NH_3 molecule as well as the confinement effect of micropores, most of the NH_3 molecules are adsorbed strongly (Figure 5a) and migrated slowly in the microporous channels (Figure 5d). At medium loading, some NH_3 molecules transport from microporous channels to mesoporous channels, and part of NH_3 molecules located in mesopores due to the micropores have already been completely occupied (Figure 5b and 5e). While at high loading, more NH_3 molecules permeate into the mesoporous channels (Figure 5c and 5f). Meanwhile, the diffusion behavior could also be quantitatively analyzed by diffusion radius,⁵⁴ and the rapid movement is generally accompanied by large diffusion radius (R_d). At low loading, as most of NH_3 molecules hop between multiple -SO₃H groups in microporous channel, R_d is small as well as diffusion is slow (Figure 5g). Interestingly, with the increase of loading, R_d is dramatically increased, and more NH_3 molecules could diffuse from microporous to mesoporous channels (Figure 5h and 5i). The same adsorption and diffusion behavior of NH_3 molecules can also be observed in OMP-SO₃H-160 (Figure S19). Overall, sequential pore-space adsorption and diffusion mechanism of NH_3 molecules inside microporous and mesoporous channels of the SOMP s has been illustrated, in which micropores preferential adsorption together with ordered mesopore subsequent storage of NH_3 , thus maximally utilizing the volume advantage of micro- and mesoporosity for NH_3 selective capture. Overall, the OMP-SO₃H-x show much better performance than industrial zeolites applied in NH_3 selective adsorption and separation, offering great opportunities for their wide applications in the field. Although the NH_3 capacity of the OMP-SO₃H-x was a little lower than few special MOFs adsorbents, but their low cost, easy preparation, and good corrosion resistance are very favorable for their scalable usage in the industry.

Conclusion

In summary, a class of stable and ordered mesoporous polymers functionalized with ample sulfonic groups were successfully developed by using the scalable and sustainable solvent-free route. The obtained SOMP s have record-high sulfonation degree (4.48 mmol/g), large BET surface areas (697 m²/g), highly ordered hexagonal mesopores combined abundantly interconnected micropores, thus possessing advantages of ideal solid adsorbents for alkaline gas capture. As expected, the SOMP s show the record integrated performance in selective adsorption and separation of NH_3 , much higher than those

of variously porous solid adsorbents reported previously. The novel inherent mechanism on sequential pore-space diffusion of NH_3 were also proposed based on both experimental results and molecular dynamics simulations. This work ignites research interest on the importance of ordered mesopores interconnected abundant micropores for corrosive gas selective capture and separation, and offers great opportunities for scalable preparation of high-capacity and low-cost porous adsorbents in the industry.

Methods

Chemicals and reagents

Resorcinol (99 wt.%), 1,4-phthalaldehyde (98 wt.%) and Pluronic F127 ($M_n=13000$) were purchased from Macklin Chemical Reagents Co. Ltd., China. NH_3 (99.99 vol.%), N_2 (99.99 vol.%) and H_2 (99.99 vol.%) were purchased from Dalian Special Gas Co. Ltd., China. All the chemicals were directly without further purification. H form ZSM-5 zeolite was supplied by Sinopec Co. Ltd.

Synthesis of SOMPs

0.44 g of resorcinol, 0.56 g of 1,4-Phthalaldehyde and 2.0 g of F127 were manually ground to achieve a uniform mixture within 5 min. The mixture was transferred to a small Teflon beaker (20 ml) and heated at 140, 160, 180, 200 or 220°C for 24 h, and reddish-brown solidified product was obtained. Then, the solidified product was dispersed in 100 mL of sulfuric acid (80 wt.%) under stirring at 80°C for 24 h, and this step was repeated for the second time. Finally, the resultant solid was filtered and washed thoroughly with hot anhydrous ethanol, and dried under vacuum at 100°C overnight. For comparison, SBA-15- SO_3H and Ce-MOF were prepared as the literatures.^{55,56}

Instruments for characterizations

X-ray diffraction (XRD) patterns were obtained on an X'Pert3 Powder diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$, $V = 45 \text{ kV}$ and $I = 40 \text{ mA}$) at a scanning rate of $1^\circ/\text{min}$. The N_2 adsorption-desorption isotherms at -196°C were measured on a Micromeritics TriStar II 3020 analyzer, and the samples were degassed under vacuum at 150°C for 6 h prior to measurements. The surface areas were calculated using the adsorption data in the relative pressure range of 0.05~0.30 according to the Brunauer-Emmet-Teller (BET) equation. The pore size distributions were calculated using the density functional theory (DFT) method, and the micropore volumes and total pore volumes were also calculated using the same method. The scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 microscope at an acceleration voltage of 5 kV. The transmission electron microscopy (TEM) images and energy-dispersive X-ray (EDX) spectroscopy elemental mapping analysis were obtained on a JEOL JEM-2010 electron microscope. The Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet iS50 spectrometer. Elemental analysis (EA) was carried out on a Vario EL III elemental analyzer. The ^{13}C solid-state nuclear magnetic resonance (NMR) spectra were collected on a Varian Inova 400 MHz spectrometer. The ^{31}P solid-state NMR spectra were obtained on a Bruker Avance III 500 MHz

spectrometer at a Larmor frequency of 202.63 MHz, and a 4 mm magic-angle-spinning (MAS) probe operated at a spinning rate of 12 kHz was used. The X-ray photoelectron spectroscopy (XPS) spectra were obtained on a Thermo ESCALAB 250XI spectrometer, and the C 1s peak at 284.8 eV was used as the standard for calibrations. The thermogravimetric analysis (TGA) curves were measured on a Netzsch STA2500 Regulus TG/DTA analyzer by heating the samples from room temperature to 850°C at a ramping rate of 10°C/min under the flowing N₂.

In-situ diffused reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were obtained on a Nicolet iS50 spectrometer equipped with an *in-situ* diffuse reflection cell. The spectra were collected with a resolution of 4 cm⁻¹ and scanning of 64 cycles. The sample was pretreated by flowing N₂ at 120°C for 1 h before each experiment. During the adsorption process, 0.05 vol.% of NH₃ balanced in N₂ was purged into the *in-situ* diffuse reflection cell at 30°C and the signal was recorded at different times. The NH₃-temperature programmed desorption (TPD) curves were measured on a Micromeritics AutoChem II 2920 analyzer connected to a Hiden HPR-20 R&D mass spectrometer. First, ~100 mg of sample was purged with He at 150°C for 2 h to remove physically adsorbed water. Then, the sample was cooled to 50°C and dosed for 30 min with 5 vol.% of NH₃ balanced in He. After being purged by He gas to eliminate the physically adsorbed NH₃, the sample was heated to 350°C at 10°C/min, under He flow of 30 mL/min. The tail gas was analyzed online by the mass spectrometer.

Gas adsorption measurements

Prior to measurements, the samples were degassed under vacuum at 150°C for 6 h. The NH₃ adsorption isotherms were measured using a self-made equipment, the accuracy of which has been validated in our previous work.^{26,57,58} The equipment is mainly composed of two stainless steel chambers connected to two pressure transducers, respectively. The amounts of NH₃ adsorbed can be calculated according to the changes of the pressures in two chambers after the samples getting in contact with NH₃. The diagram for the equipment and detailed measuring procedures are presented in the Supporting Information (see Scheme S1 and related description). The N₂ and H₂ adsorption isotherms at 25°C were measured on a Micromeritics TriStar II 3020 analyzer mentioned above.

Breakthrough curves for NH₃/N₂/H₂ mixed gas adsorption were measured on a Micromeritics AutoChem II 2920 analyzer connected to a Hiden HPR-20 R&D mass spectrometer. All the measurements were conducted using a U-type quartz tube (6 mm inner diameter × 190 mm length). In a typical run, a certain amount of sample (~100 mg) was fixed in the quartz tube; the sample was first purged with He flow (30 mL/min) at 150 °C for 3 h to remove any volatile residues; the temperature was then cooled down to the target temperature of 25 or 50 °C, and the He flow was switched to 5v%NH₃/23.75v%N₂/71.25v%H₂ mixed gas flow (20 mL/min) for competitive adsorption. The composition of inlet gas was controlled by mass flowmeters. The compositions of outlet gas were measured online by the mass spectrometer. To evaluate the water resistance of OMP-SO₃H-180, the sample was firstly treated with saturated water vapor at 50°C for 2 h, which was then performed the above breakthrough test.

Mesoporous adsorption measurements

The NH₃ adsorption measurement in the mesopores of SOMP were carried out with the following procedures: NH₃ was firstly adsorbed on SOMP until saturation in both micropores and mesopores area, then the samples were controllably degassed under vacuum at 80°C for 6 h to selective removal of adsorbed NH₃ in the mesopores of SOMP. Afterwards, the second NH₃ adsorption measurement of the treated SOMP was performed that can reveal the mesopores adsorption behavior of SOMP.

Molecular dynamics simulation

Molecular dynamics simulations can provide a better understanding about the adsorption and diffusion of small molecules in porous materials.^{59–60} In this work, the adsorption and diffusion of NH₃ in two synthesized SOMP (OMP-SO₃H-160 and OMP-SO₃H-180) were studied. Firstly, the initial framework structures (C₁₀₅₀₀H₉₀₁₀O₅₀₀₀S₁₀₀₀) were built according to experimental densities (0.3731 and 0.3053 g/cm³), and the lattice parameters were set to 110.4×110.4×110.4 Å³ for OMP-SO₃H-160 and 103.2×103.2×103.2 Å³ for OMP-SO₃H-180, respectively. To determine the adsorption and diffusion property of NH₃ at different loadings, the number of NH₃ molecules were 469 (0.001 bar), 1837 (0.12 bar) and 3361 (1.0 bar) for OMP-SO₃H-160, as well as 100 (lower than 0.004 bar), 2040 (0.12 bar) and 3726 (1.0 bar) for OMP-SO₃H-180, corresponding to low, medium and high loadings of NH₃, respectively, based on the experimental NH₃ adsorption isotherms. All the molecular dynamics simulations were performed in the canonical ensemble (NVT), where the number of particles (N), simulation volume (V) and temperature (T) were kept constant. The temperature was held at 298 K and controlled by a Nosé-Hoover thermostat with a coupling time of 1 ps. The velocity Verlet algorithm was used throughout to integrate the Newton's equations of motion. During the simulations, periodic boundary condition was applied in all three directions. All the interactions were modeled using the COMPASS force field, which have been widely applied in porous materials.^{61–65} The van der Waals potential was truncated and shifted at the distance of 12.5 Å, and the electrostatic energy was calculated by the Ewald summation method.⁶⁶ Each molecular dynamics simulation was run for 5×10⁶ equilibration steps with 1 fs of timestep. Then, a production run of 1×10⁷ steps was performed. The trajectories were recorded every 1000 steps to analyze the adsorption and diffusion behavior. Simulations were performed in HPC resources of SINOPEC and Shenzhen Cloud Computing Center.

Declarations

Additional Information

Supplementary information accompanies this paper at <http://www.nature.com/naturecommunications>.

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Author Contributions

X. Kan and F.-Y. Li synthesized the SOMPs samples, analyzed the results and performed all the tests. Z.-Q. Liu, W. Chen and X.-F. Yi. designed molecular dynamics simulation. K. Huang and F.-J. Liu conceived the idea, proposed the strategy and draft the manuscript. F.-J. Liu gave the foundation support. A.-M. Zheng, L.-L. Jiang and F.-S., Xiao supervised the project, helped design the experiments, evaluated the data. All authors discussed the results and co-wrote the manuscript.

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Scheme 1

Scheme 1 is available in the Supplementary Files section.

Figures

Figure 1

(a) Small-angle XRD patterns, (b) N₂ adsorption-desorption isotherms at -196 °C and (c) pore size distribution of the SOMPs; (d, e) SEM, (f, g) TEM images with corresponding electron diffraction patterns (inside), (h) STEM images and (i~k) elemental maps of the OMP-SO₃H-180. N₂ sorption isotherms for OMP-SO₃H-180, OMP-SO₃H-160 are offset by 300 and 700 cm³/g along vertical axis for clarity. The pore

size distributions of OMP-SO₃H-180, 200 are offset by 0.125 and 0.275 cm³/g along vertical axis for clarity.

Figure 2

(a) ¹³C solid-state NMR spectra, (b) ³¹P solid-state NMR spectra of adsorbed TMPO probe molecule, (c) O1s XPS spectra, and (d) S2p XPS spectra of various SOMPs.

Figure 3

NH₃ sorption isotherms of the SOMP materials at (a) 25 °C and (b) 50 °C; IAST selectivities of the SOMP materials for (c) NH₃/N₂ and (d) NH₃/H₂ at 25 °C; breakthrough curves for NH₃/N₂/H₂ mixed gas (20 mL/min) by OMP-SO₃H-180 at (e) 25 °C and (f) 50 °C.

Figure 4

(a) Cycling of OMP- SO_3H -180 for NH_3 adsorption; (b) *in-situ* DRIFTS spectra of OMP- SO_3H -180 for NH_3 capture at 25 °C; (c) NH_3 -TPD MS curve of OMP- SO_3H -180; (d) NH_3 isotherms of fresh and mesopore desorbed OMR- SO_3H -180 at 25 °C.

Figure 5

(a~c) Adsorption and diffusion of NH_3 molecule in the OMP- SO_3H -180 at various loadings; (d~e) adsorption snapshot, (d~f) diffusion trajectory, and (g~i) diffusion radius for NH_3 at (a, d, g) low, (b, e, h) medium and (c, f, i) high loadings. The red and blue areas are microporous and mesoporous channels, respectively. The black balls represent N atoms (H atoms in NH_3 are omitted for clarity). Insets in Figure 5g and h are schematics of molecule diffusing in microporous and mesoporous channels, respectively.

Supplementary Files

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