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A novel mechanochemical method for reconstructing the moisture-degraded HKUST-1†

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A novel mechanochemical method was proposed to reconstruct quickly moisture-degraded HKUST-1. The degraded HKUST-1 can be restored within minutes. The reconstructed samples were characterized, and confirmed to have 95% surface area and 92% benzene capacity of the fresh HKUST-1. It is a simple and effective strategy for degraded MOF reconstruction.

Metal–organic frameworks (MOFs) have received widespread attention owing to their ultrahigh specific area, tunable pore size and adjustable surface functionality.[1,2] MOFs showed great promises in a variety of applications including gas adsorption and separation.[3,4] Despite their potential as absorbent materials, some of the most developed MOFs (e.g. HKUST-1) are moisture-sensitive because the relative weak metal–oxygen coordination was readily broken by water molecules when exposed to moisture, resulting in the phase transformation and decomposition of the framework.[5] This drawback greatly hinders their industrial applications. To resolve the issue, some approaches have been proposed to enhance the hydrophobicity of MOFs including choosing organic ligands with hydrophobic groups and grafting hydrophobic functional groups (e.g. alkyl or fluoro chains) into their frameworks.[6,7] However, these approaches present shortcomings such as uneven grafting, low grafting rate and high costs. Moreover, the degraded MOF materials are hazardous due to the composition of heavy metals and aromatic compounds, which cause secondary pollutions if not recycled properly. Therefore, the efficient regeneration of degraded MOFs is worthy of further investigation. However, few regeneration methods of degraded MOFs were developed successfully.

HKUST-1 (Cu-BTC, MOF-199) is a type of ideal adsorbent for VOCs and CO_2 adsorption at normal temperature and pressure, which is obtained via green and low-cost synthesis with high yield, but readily degraded under humid conditions.[8,9] Majano et al.[10] reconstructed the degraded HKUST-1 in liquid/gas phase ethanol. However, long treatment time (over 5 h) and a large amount of ethanol solvent (up to 40 mL g^{-1}) were used in regeneration. Therefore, it is worth further exploring an efficient method to reconstruct degraded HKUST-1.

In recent years, there was considerable interest in the mechanochemical synthesis of MOFs.[11,12] For example, Yuan et al.[13] and Yang et al.[14] successfully synthesized HKUST-1 by mechanochemical synthesis. In addition, Yuan et al.[15] also reported that MOFs could completely be transformed into some other MOFs with different topologies by grinding with small amounts of liquid, and thought that the lability of MOFs under grinding conditions could be exploited synthetically and for regenerating materials which have lost crystallinity.

Herein, we initiated a novel mechanochemical ball-milling method to fast reconstruct the degraded HKUST-1. The degraded HKUST-1 can fully be reconstructed within minutes by grinding with small amounts of solvent (Fig. 1). For further comparison, we also reconstructed the degraded sample by the
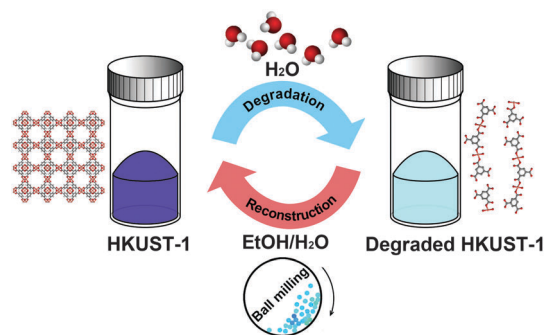
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Fig. 1 Solvent-assisted mechanochemical reconstruction of the degraded HKUST-1.
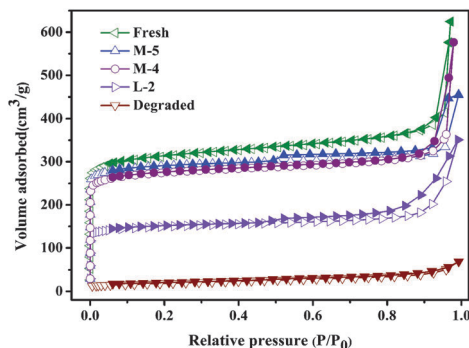
Fig. 2 At 77 K, isotherms of N_2 on the fresh HKUST-1, the degraded HKUST-1 and reconstructed samples after treatment for 30 min. (The open symbols refer to the adsorption isotherms, and the solid symbols represent the desorption isotherms.)

liquid immersion method.[10] In addition, the textural structure and benzene vapor adsorption of the reconstructed samples were examined.

Fig. 2 and Fig. S1 (ESI†) show N_2 adsorption–desorption isotherms of the samples fresh HKUST-1, degraded HKUST-1 and reconstructed HKUST-1 at 77 K. It can be seen that the N_2 isotherms of the degraded HKUST-1 sharply became low in comparison with the fresh HKUST-1. After reconstruction of the degraded HKUST-1 by the proposed mechanochemical method, the N_2 isotherms of all the reconstructed samples became higher compared to those of the degraded HKUST-1 sample. It was noticed that N_2 isotherms of the samples M-5 and M-4 became close to that of the fresh HKUST-1. However, the N_2 isotherms of M-5 exhibit a type-H4 hysteresis loop in the IUPAC classification.[16] It indicated that the M-5 sample contained mesopores in the form of cracks and fissures, besides micropores.[13] Table 1 summarizes the specific treatment conditions for reconstructing the degraded HKUST-1 and the textural properties of these reconstructed samples. It indicated that the BET surface area of the degraded HKUST-1 was only 66.2 m^2 g^{-1}, much lower than that of the fresh HKUST-1 (S_{BET} = 1215.1 m^2 g^{-1}). In contrast, BET surface areas of all the reconstructed samples improved. Among the reconstructed samples, M-5 showed the highest recovery of 95% with a BET surface area of 1150.8 m^2 g^{-1} and a total pore volume of 0.52 cm^3 g^{-1}. It was worthy of mention that the relative standard deviation of BET surface area of these reconstructed samples was below 2%, showing good repetitiveness. Noteworthily, it only needed 30 min to finish reconstruction of the degraded HKUST-1. In contrast to that, L-2 prepared by the conventional liquid immersion method (using large amounts of solvent) showed a lower recovery of 48%, having a BET surface area of 585.6 m^2 g^{-1}. Therefore, mechanochemical reconstruction was an effective method to reconstruct the degraded HKUST-1. It could be ascribed to following reasons. One is that the kinetic energy supplied during grinding can have several positive effects on solid reactants including: heating, reduction of particle size, formation of defects and dislocations in crystal lattices, local melting and even phase changes to alternative polymorphs.[14]

The second is that solvent can enhance the mobility of the degraded material, which could in turn help to enhance the rate of mass transfer during HKUST-1 reconstruction.[17] In the end, these effects could greatly promote the course of mechanochemical crystallization.

The crystalline structures of the fresh HKUST-1, the degraded HKUST-1 and the reconstructed samples were verified using X-ray diffraction (see Fig. S2, ESI†). The degraded HKUST-1 showed a completely different pattern from that for the fresh HKUST-1. The reconstructed samples (M-4 and M-5) showed the same XRD patterns as that of the fresh HKUST-1. It was also noticed that compared to the liquid immersion reconstructed samples (L-1 and L-2), the mechanochemically reconstructed samples (M-3 and M-4) showed higher crystallinities (with stronger peak intensities) with the same treatment time, in agreement with the higher BET surface areas of M-3 and M-4 indicated in Table 1, suggesting that the mechanochemical method was an efficient method for the reconstruction of the degraded HKUST-1.

Fig. S3 (ESI†) shows the SEM images of the fresh HKUST-1, the degraded HKUST-1 and the reconstructed samples. Fig. S3a (ESI†) exhibits the octahedral structure of fresh HKUST-1. After HKUST-1 was attacked with moisture, its octahedral structure was degraded to the layered structure, as shown in Fig. S3b (ESI†). The layered crystals were comprised of several different phases including a layered [$Cu_2OH(BTC)(H_2O)$] compound.[10,18] Fig. S3h,i (ESI†) exhibit the SEM images of the reconstructed HKUST-1 samples, which were similar to that of the fresh HKUST-1. Noteworthily, no layered structure representing the degraded HKUST-1 was observed. It implied that the layered crystals (the degraded HKUST-1) have been reconstructed to HKUST-1 crystals. The mechanism involved in the reconstruction process of moisture-degraded HKUST-1 may be as follows: when a solvent-assisted mechanochemical method was applied to reconstruct the degraded HKUST-1, the kinetic energy supplied during grinding leads to reduction of layered crystal size, the breakage of intramolecular bonds and the lattice defects and dislocations of layered crystals.[14] Meanwhile, the EtOH and EtOH–H_2O mixtures used in the reconstruction process would disturb H-bonding between neighboring trimesic acid molecules and thus enhance their flexibility/mobility for coordination to nearby Cu atoms, which would in turn help to destabilize the Cu–O chains of layered crystals for facilitating successive reconstruction steps.[10] As a consequence of this, the layered crystals (the degraded HKUST-1) are rapidly reconstructed to HKUST-1 crystals.

In addition, remarkable morphology changes were observed for the reconstructed HKUST-1 samples prepared by different methods. A comparison of Fig. S3d and i (ESI†) shows that the mechanochemically reconstructed sample M-5 showed smaller particle size and less defined crystalline features compared to the reconstructed sample L-2, as the reduction of particle size and formation of defects occurred during grinding. In addition, for the mechanochemically reconstructed samples, their layered crystal structures gradually disappeared along with an increase in the amount of solvent, as shown in Fig. S3e–g (ESI†), indicating

Table 1 Summary of various treatment conditions for reconstructing the degraded HKUST-1 and the textural properties of these reconstructed samples

Sample	Reconstruction method	Solvent used	Ratio of solvent to reactant (mL g^{-1})	Treatment time (min)	BET (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	
						Total	Micropore
Fresh HKUST-1	—	—	—	—	1215.1	0.60	0.38
Degraded HKUST-1	—	—	—	—	66.2	0.07	0
M-1	Mechanochemical	EtOH	0.4	15	334.4	0.24	0.09
M-2	Mechanochemical	EtOH	1.2	15	664.0	0.40	0.22
M-3	Mechanochemical	EtOH	2.0	15	820.3	0.42	0.27
M-4	Mechanochemical	EtOH	2.0	30	1081.1	0.54	0.36
M-5	Mechanochemical	EtOH–H$_2$O	2.0	30	1150.8	0.52	0.39
L-1	Liquid immersion	EtOH	80	15	462.0	0.32	0.12
L-2	Liquid immersion	EtOH	80	30	585.6	0.36	0.19

that the addition of a minor amount of solvent could enhance the formation of crystalline HKUST-1, consistent with the BET and XRD results.

FTIR spectra of the fresh HKUST-1 and the reconstructed M-5 show high similarities (Fig. S4, ESI†). Both samples exhibit the characteristic asymmetric stretching vibrations of carboxylate groups at 1645/1585 cm^{-1} and the symmetric vibrations at 1456/1376 cm^{-1}.[19] It indicated that the reconstructed M-5 has exactly the same coordination type of the carboxylate groups and metal cations as that for the fresh HKUST-1, suggesting that the reconstructed M-5 is indeed the HKUST-1 product.

The thermal stability of the fresh HKUST-1 and the reconstructed sample M-5 was evaluated by the thermogravimetric (TG) and derivative thermogravimetric (DTG) analysis (Fig. S5, ESI†). The reconstructed M-5 showed similar thermal stability to that for the fresh HKUST-1. Their DTG curves showed a small peak below 373 K, which can be attributed to the desorption of physically adsorbed water. Then, the sharp peak appeared at about 581 K, corresponding to the decomposition of the BTC ligand.

Fig. 3 shows isotherms of benzene vapor at 298 K on the samples. The degraded HKUST-1 sample has hardly adsorption capacity of benzene vapor at $P < 40$ mbar because of a complete collapse of the HKUST-1 framework. At $P > 40$ mbar its adsorption amount of benzene vapor increased with pressure, which was related to the intermolecular benzene–benzene interactions. In contrast to this, the isotherms of benzene on the reconstructed HKUST-1 were greatly higher than that on the

degraded HKUST-1, and the isotherm of benzene on the M-5 sample was close to that on the fresh HKUST-1. For comparison, Table S1 (ESI†) lists the benzene vapor adsorption capacities of some adsorbents studied in this work and reported by some investigators. It indicated that their amounts adsorbed of benzene followed the order of L-2 < M-4 < M-5 < fresh HKUST-1, which was consistent with the order of the surface area of these samples. The benzene adsorption capacities of M-5 and L-2 at 298 K and 100 mbar were 5.7 and 3.5 mmol g^{-1}, which showed 92% and 56% recovery, respectively, suggesting that the mechanochemical method is more efficient than the liquid immersion method. In addition, the fresh HKUST-1 and the reconstructed M-5 sample showed higher benzene adsorption capacities than those of conventional adsorbents such as activated carbon and zeolites. It was also noticed that at high pressure (100 mbar), the benzene adsorption capacities of the fresh HKUST-1 were lower than that of MIL-101, but at low pressure (2.5 mbar), it was 3.1 times that of MIL-101. It could be mainly attributed to the rich micropores of the fresh HKUST-1, whose micropore volume was up to 0.38 cm^3 g^{-1}. Moreover, its micropore sizes are smaller than those of MIL-101, resulting in higher adsorption affinity towards some VOCs. Reconstructed HKUST-1 similarly exhibited excellent adsorption behavior for VOCs at low concentration, and thus is considered as one of the promising candidates for VOC removals.

In summary, a solvent-assisted mechanochemical method was successfully developed for the reconstruction of moisture-degraded HKUST-1. The moisture-degraded HKUST-1 can be restored within 30 minutes. The reconstructed samples were confirmed to have 95% surface area and 92% benzene capacity of the fresh HKUST-1, much higher than those of the reconstructed samples prepared by the conventional liquid immersion method. The mechanochemical approach demonstrated in this work may provide an effective strategy for the reconstruction of some moisture-degraded MOFs for industrial applications.
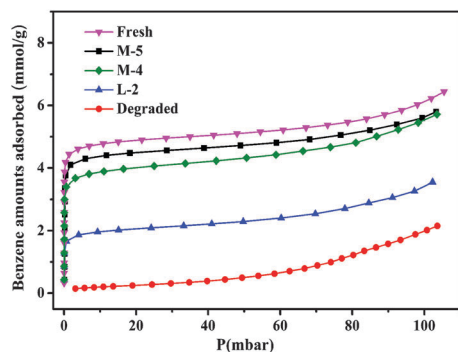
Fig. 3 Adsorption isotherms of benzene vapor at 298 K on the fresh HKUST-1, the degraded HKUST-1 and the reconstructed samples.

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