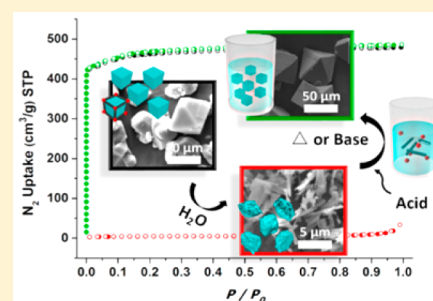


Simple and Efficient Regeneration of MOF-5 and HKUST-1 via Acid–Base Treatment

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S Supporting Information

ABSTRACT: Simple and efficient regeneration of MOF-5 and HKUST-1 is demonstrated via acid–base treatment. The reactants are recovered simply by dissolving the deteriorated MOFs in strong acid. Pristine MOFs are regenerated in high yields by adjusting the solution pH via either *in situ* base formation or *ex situ* base addition. Both regeneration protocols are environmentally benign and cost-effective because the reactants in the deteriorated MOFs are recycled. Especially the *ex situ* base addition protocol can be done in a cheap and environmentally friendly ethanol/water mixed solvent at ambient condition and is suitable for large-scale batch regeneration owing to the simple procedure and short reaction time.



■ INTRODUCTION

Metal–organic frameworks (MOFs) have attracted significant attention because of their potential as gas capture, separation, and storage materials.^{1–6} However, the limited durability and high preparation cost of MOFs hinder their application, although some have promising properties. For large-scale applications, it becomes important either to synthesize new MOFs inexpensively or to develop inexpensive protocols for producing known MOFs. Recycling is an option for cheaply and efficiently preparing a known MOF, because the MOF precursors can be recovered from the degraded or deteriorated material. It is important to establish such a regeneration protocol both in a batch mode and at bulk scale.

MOF-5, one of the most widely studied MOFs, has a large pore volume and a large surface area. However, its practical application is limited by its instability under ambient conditions.^{7–9} HKUST-1 is reported to have the largest volumetric capacity for CH₄ delivery¹⁰ and the second largest working capacity for CO₂ capture via the pressure swing adsorption process¹¹ after HB-d.¹² The hydrothermal stability of HKUST-1 is superior to that of MOF-5 but is still not adequate for extended use.^{9,13,14} The limited durability of HKUST-1 under hygroscopic conditions increases the operational cost of systems employing this MOF. Majano et al. have reported a facile one-step approach for regenerating degraded HKUST-1.¹⁴ Ethanol treatment of degraded HKUST-1 in a fixed-bed reactor produced up to 94% porosity recovery. However, their batch mode regeneration of HKUST-1 was not as efficient as *in situ* regeneration. Sun et al. proposed a mechanochemical method for regenerating HKUST-1.¹⁵ Although the porosity of the recovered HKUST-1 was as much as 95% of that of fresh, mechanochemically prepared HKUST-1, the BET surface area of the recovered material was

only ~60% of that reported for pristine HKUST-1 synthesized by solvothermal reaction.

We demonstrate herein simple and efficient protocols for recycling MOF-5 and HKUST-1, where the reactants are recycled from the corresponding degraded or deteriorated MOF. The reactants can be recovered simply by dissolving the degraded or deteriorated MOF in a strong acid (Figure 1). Because the acidic solution of an MOF contains a metal ion and

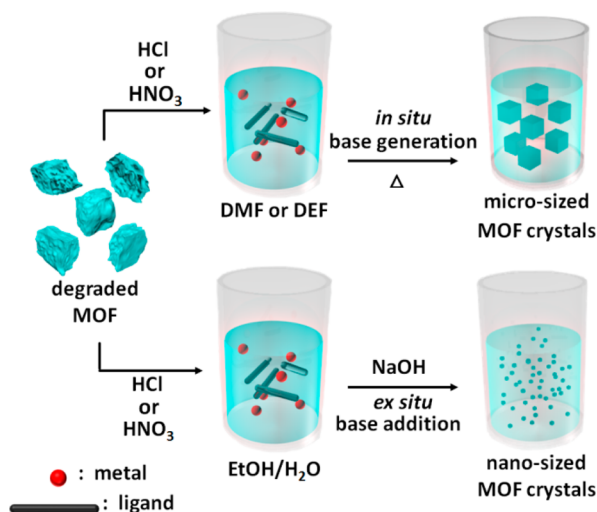


Figure 1. Regeneration of MOFs via dissolution of degraded MOFs in strong acid and subsequent pH adjustment using either *in situ* generated or *ex situ* added base.

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a ligand in the exact stoichiometric ratio of the corresponding MOF, appropriate pH control of the solution could lead to the regeneration of a pristine MOF. The solution pH can be adjusted either by *in situ* production or *ex situ* addition of base. When an amide-based solvent such as *N,N*-dimethylformamide (DMF) or *N,N*-diethylformamide (DEF) is used for regeneration, the base (dimethylamine or diethylamine) is generated *in situ* via solvent decomposition during the reaction. The *ex situ* addition of base serves the same role in controlling the solution pH during the regeneration of the MOF.

■ EXPERIMENTAL SECTION

Materials and Methods. All chemicals used in this work were purchased from commercially available sources and used without further purification. Basolite C300 (HKUST-1) was purchased from Sigma-Aldrich. Powder X-ray diffraction (PXRD) data were collected on a Bruker D2 PHASER. Infrared (IR) spectra were measured using a ThermoFisher Scientific iS10 FT-IR spectrometer. Field emission scanning electron microscope (SEM) images were taken using a FEI Nova NanoSEM 230 instrument. N_2 sorption isotherms were measured at 77 K with ASAP 2020 (Micromeritics Instrument Corp.) by a standard volumetric technique up to 1 atm.

Preparation of MOF-5. MOF-5 was prepared according to a slight modification of a reported procedure.¹⁶ $Zn(NO_3)_2 \cdot 6H_2O$ (0.75 g (2.5 mmol)) and 1,4-benzenedicarboxylic acid (H_2BDC ; 0.20 g (1.2 mmol)) were added to a 125 mL jar with 50 mL of DEF. The solution was heated in a 100 °C oven for 2 days. After the solution was cooled to room temperature, the solvent was decanted. The crystalline product was washed several times with anhydrous DMF and anhydrous methylene chloride. The product was dried at 150 °C in a vacuum oven overnight (yield = 0.28 g, 91%).

Preparation of HKUST-1. HKUST-1 was prepared according to a published procedure.¹⁷

Degraded MOF-5. Vacuum dried MOF-5 was soaked in distilled water for 1 day with stirring. The degraded sample was kept in an oven at 60 °C until it was completely dry.

Degraded HKUST-1. Four different kinds of degraded HKUST-1 samples were prepared by two slightly different procedures using two different source materials, the as-synthesized HKUST-1 and commercially obtained Basolite C300. As-synthesized HKUST-1 (or Basolite C300; 2 g) was transferred into 80 mL of water, and the solution was stirred for either 1 day under ambient conditions or 6 h at 100 °C. The four different degraded samples were dried overnight at 100 °C in an oven.

Preparation of a Mixed Degraded HKUST-1 Sample. Four different solutions containing degraded HKUST-1 from two different sources subjected to two different degradation procedures were combined and dried at 100 °C in an oven overnight to obtain a mixed degraded sample.

Regeneration of MOF-5 via *in Situ* Base Formation. MOF-5 (0.25 g) predried under vacuum at 150 °C was transferred into water (50 mL), and the solution was stirred for 1 day. The degraded sample was kept in an oven at 60 °C until it was completely dry. The dried sample was dissolved in DEF (50 mL) containing HNO_3 (0.2 mL, 70% (w/w)). The mixture was sonicated for several minutes and kept in a 100 °C oven for 2 days. After the solvents were decanted, the product was soaked in fresh DMF and the solvent was refreshed five times over 1 day. The same procedure was repeated using methylene chloride. The product was dried under vacuum at 150 °C overnight (yield = 0.22 g, 85%).

Regeneration of HKUST-1 via *in Situ* Base Formation. Basolite C300 (1.00 g) predried under vacuum at 120 °C was transferred into water (50 mL), and the solution was stirred for 1 day. The degraded sample was kept in an oven at 100 °C until completely dry. The dried sample was dissolved in HNO_3 (or HCl) solution (1 M, 10 mL), and a DMF/EtOH/ H_2O (50 mL, 2:2:1 volume ratio) mixed solvent was added to the solution while stirring. The solution was kept in an oven at 70 °C for 1 day. The solvent was repeatedly refreshed with DMF

and acetone for 2 days. The product was dried at 120 °C under vacuum for 1 day. The regeneration yield was 0.87 g (87%) from the nitric acid solution and 0.70 g (70%) from the hydrochloric acid solution.

Regeneration of HKUST-1 via *ex Situ* Base Addition. Basolite C300 (1.00 g) predried under vacuum at 120 °C was transferred into water (50 mL), and the solution was stirred for 1 day to yield a light blue powder. The powder was dried at 70 °C in an oven overnight. After dissolving the dried sample in a 1 M HCl solution (20 mL), an EtOH/ H_2O (80 mL, 1:1 volume ratio) mixed solvent was added to the solution. Addition of 1 M NaOH solution (15 mL, 20 mL, and 25 mL quantities of 1 M NaOH representing acid–base ratios of 1:0.75, 1:1, and 1:1.25, respectively) resulted in immediate precipitation. After stirring the solution for an additional 1 h, the precipitate was filtered and washed several times with ethanol. The product was dried under vacuum overnight at 120 °C producing the following regeneration yields at HCl:NaOH ratios of 1:0.75 (0.38 g, 38%), 1:1 (0.87 g, 87%), and 1:1.25 (0.63 g, 63%).

Regeneration of HKUST-1 from a Mixture Consisting of Four Different Deteriorated HKUST-1 Samples. After dissolving the mixture (8.0 g) containing the four different degraded HKUST-1 samples (2 g each) in a 1 M HCl solution (140 mL), an EtOH/ H_2O mixed solvent (160 mL, 1:1 volume ratio) was added to the solution while stirring. After removal of a small amount (less than ~1 mg) of undissolved solid, a NaOH solution (140 mL) was slowly added to the solution for 5 min while stirring. After an additional 1 h stirring, the precipitate was filtered, washed several times with ethanol, and dried under vacuum overnight at 120 °C (regeneration yield = 7.4 g, 93%).

Regeneration of HKUST-1 in the Presence of Additional Cu(II) Ions. Because there have been several reports on HKUST-1 synthesis with Cu(II) ion to 1,3,5-benzenetricarboxylic acid (H_3BTC) ratio larger than the stoichiometric ratio in HKUST-1,^{18–21} regeneration reactions were carried out with the addition of up to ~30% more Cu(II) ions to the solution. However, no meaningful increases in recovery yield were observed.

■ RESULTS AND DISCUSSION

Regeneration of MOF-5 via *in Situ* Base Formation.

Pristine MOF-5 is regenerated via solvothermal reaction in DEF using a deteriorated MOF-5 sample dissolved in nitric acid solution. The SEM images of the samples support the degradation and regeneration of MOF-5 (Supporting Information (SI) Figure S1). The PXRD patterns and IR spectra of regenerated MOF-5 confirm the regeneration of pristine MOF-5 from degraded MOF (Figure 2a and SI Figure S2). The 85% recovery yield is comparable to that of as-synthesized MOF-5 (91% yield). The N_2 sorption behavior of regenerated MOF-5 supports the complete recovery of porosity (Figure 2b). The BET surface area of regenerated MOF-5, 3480 m² g^{−1}, is comparable to that of as-synthesized MOF-5 (3520 m² g^{−1}). An attempt to regenerate MOF-5 using hydrochloric instead of nitric acid was not successful. A similar observation has been reported in the literature.¹⁶ While the solvothermal reaction of 1,4-benzenedicarboxylic acid (H_2BDC) with $Zn(NO_3)_2$ yields MOF-5, a similar reaction with anhydrous $ZnCl_2$, which does not contain any nitrate ion, produced an unidentified amorphous product.¹⁸

Regeneration of HKUST-1 via *in Situ* Base Formation.

The protocol used for the regeneration of MOF-5 was also applied to the regeneration of HKUST-1. After dissolving degraded or deteriorated HKUST-1 in strong acid solution, solvothermal reaction in mixed DMF/ethanol/water solvent resulted in micrometer-sized HKUST-1 crystals (Figure 3). Both the structural characteristics and porosity of the MOF are recovered via a solvothermal reaction in a solution containing DMF as an *in situ* source of base (Figure 4 and SI Figure S3).

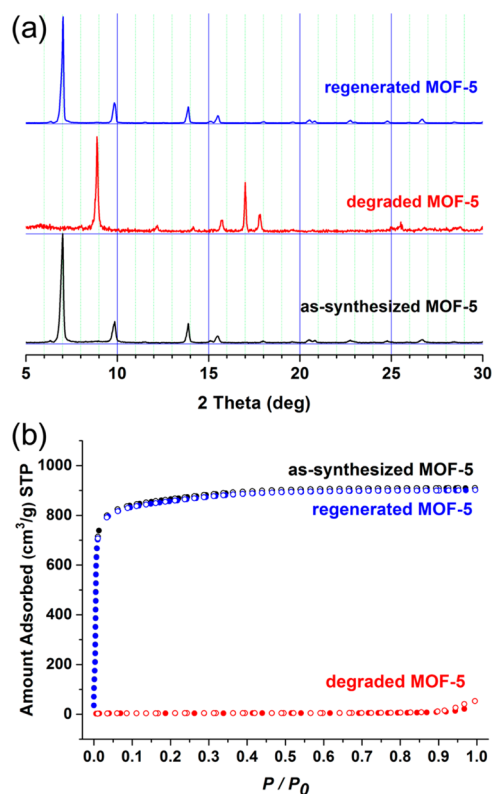


Figure 2. (a) PXRD patterns of as-synthesized MOF-5 (black), degraded MOF-5 (red), and regenerated MOF-5 (blue). (b) N₂ sorption isotherms of as-synthesized MOF-5 (black), degraded MOF-5 (red), and regenerated MOF-5 (blue).

The N₂ sorption isotherms of regenerated HKUST-1 are the same as that of Basolite C300, regardless of the kind of strong acid used for the dissolution of degraded Basolite C300 (Figure 4b). The BET surface area of HKUST-1 regenerated from a solution containing either nitric acid or hydrochloric acid equals 1820 or 1840 m² g⁻¹, respectively, which is the same as that of Basolite C300 (1840 m² g⁻¹). However, the kind of acid slightly affects the recovery yield. The recovery of HKUST-1 from the nitric acid solution is ~90%, whereas that from the hydrochloric acid solution is only ~70%.

Regeneration of HKUST-1 via *ex Situ* Base Addition.

The solvothermal reactions for regenerating MOF-5 and HKUST-1 entail high synthetic cost due to their high reaction temperatures and lead to concerns owing to the use of environmentally harmful amide-based solvents. HKUST-1 can also be regenerated from a strongly acidic solution without the use of amide-based solvents simply by adjusting the solution pH to a value appropriate for network formation by *ex situ* addition of base. The IR spectrum of HKUST-1 regenerated by *ex situ* base addition is the same as that of Basolite C300 (Figure S4). As in the *in situ* regeneration procedure, deteriorated HKUST-1 was first dissolved in a strong acid such as HCl, after which the solution pH was adjusted by the addition of an appropriate amount of NaOH (Figure 5). Even if the amount of the base added is significantly less than 1 equiv of the acid used to dissolve the deteriorated HKUST-1, the material is regenerated. The PXRD pattern of HKUST-1 regenerated by the addition of 0.75 equiv of base is the same as that of pristine HKUST-1 (Figure 5a). The porosity of the regenerated material is also the same as that of pristine HKUST-1 (Figure 5b). However, the recovery yield of HKUST-1 is only 38%. When an equivalent amount of the

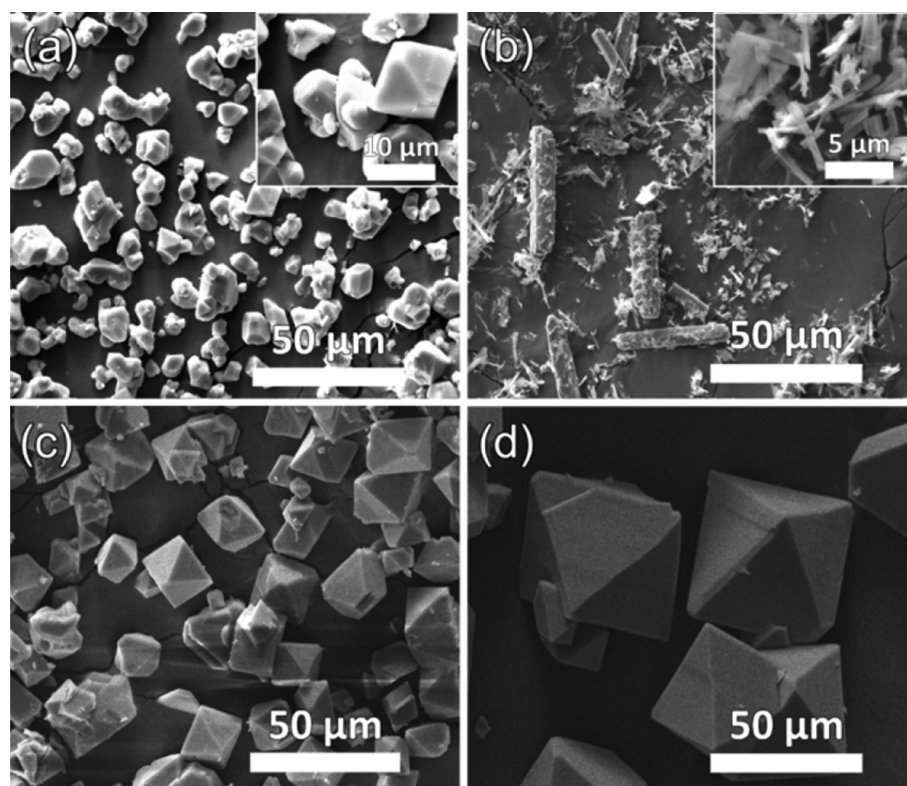


Figure 3. SEM images of (a) Basolite C300, (b) degraded Basolite C300, (c) regenerated HKUST-1 from a solution containing nitric acid, and (d) regenerated HKUST-1 from a solution containing hydrochloric acid.

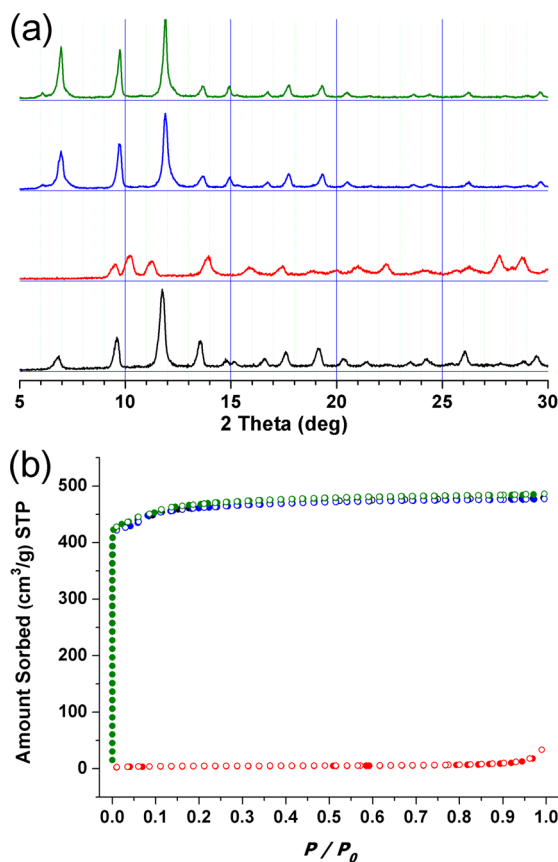


Figure 4. (a) PXRD patterns and (b) N₂ sorption isotherms of Basolite C300 (black), degraded Basolite C300 (red), regenerated HKUST-1 from a solution containing nitric acid (blue), and regenerated HKUST-1 from a solution containing hydrochloric acid (green).

base is added, the recovery yield reaches its greatest value of 87%. On the other hand, when the amount of the base added is significantly greater than 1 equiv, HKUST-1 is not regenerated. The PXRD pattern of the crystalline product obtained by the addition of 1.25 equiv of sodium hydroxide is different from that of pristine HKUST-1. The BET surface area calculated from the N₂ adsorption isotherm on the unidentified crystalline product is only 270 m² g⁻¹. Even though the size of the regenerated HKUST-1 crystals obtained via *ex situ* base addition is much smaller than that of the crystals obtained via *in situ* base formation (SI Figure S5), the BET surface areas of both regenerated HKUST-1 samples are the same as that of pristine HKUST-1 regardless of the regeneration procedure. As in the regeneration of HKUST-1 by *in situ* base formation, regeneration by *ex situ* base addition is not affected by the kind of strong acid used for the dissolution of deteriorated HKUST-1. While the reconstruction of MOF-5 exhibits an acid dependency, HKUST-1 can be regenerated regardless of the type of strong acid used for the dissolution of degraded MOF. Thus, HKUST-1 can be regenerated from deteriorated material dissolved using HNO₃ (SI Figures S6–S8). It is worth mentioning that regeneration via *ex situ* base addition is very fast. The reaction can be completed within 1 min, although all HKUST-1 regeneration reactions in this study were carried out for 1 h. The recovery yield and all properties including the porosity of HKUST-1 obtained within 1 min are comparable to those of HKUST-1 obtained after 1 h (SI Figures S9–S12).

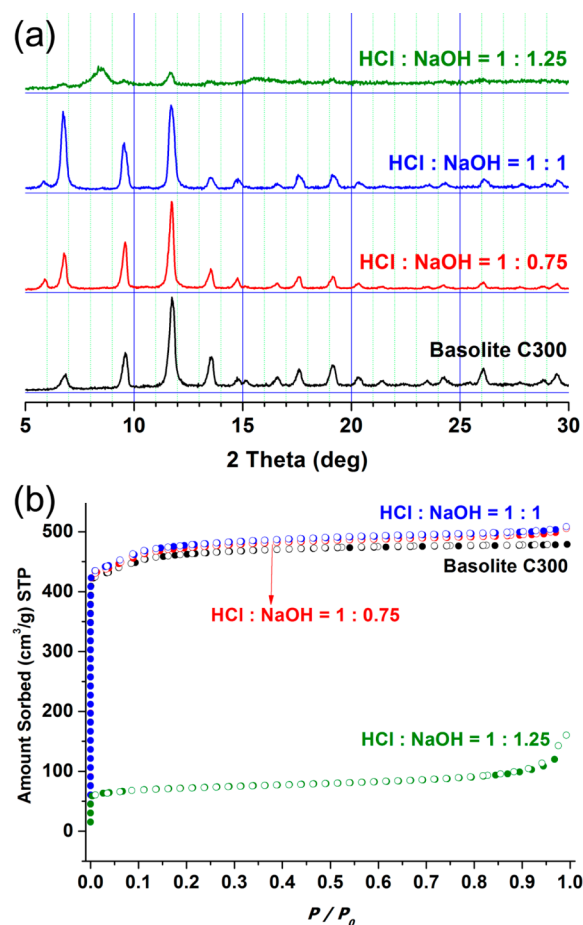


Figure 5. (a) PXRD patterns and (b) N₂ sorption isotherms of Basolite C300 (black) and regenerated HKUST-1 samples from reaction conditions employing hydrochloric acid to sodium hydroxide ratios of 1:0.75 (red), 1:1 (blue), and 1:1.25 (green), respectively.

Regeneration of HKUST-1 from a Mixture Consisting of Four Different Deteriorated HKUST-1 Samples.

To examine the sample dependency of regeneration, four different deteriorated HKUST-1 samples were prepared using HKUST-1 from two different sources subjected to two different deterioration processes. As-synthesized HKUST-1 was prepared according to the procedure reported by Xiang et al.¹⁷ Basolite C300 was used as obtained. The deteriorated samples were prepared either by soaking HKUST-1 in water for 1 day at ambient temperature or by refluxing HKUST-1 in water for 6 h. Regeneration was performed via *ex situ* base addition to a mixture containing equivalent amounts of four different deteriorated HKUST-1 samples. An 8 g amount of the mixture was dissolved in hydrochloric acid solution, which was chosen as a strong acid to avoid the potential risk of explosion of nitrate ion when used in bulk quantity. Crystalline HKUST-1 was regenerated in ~92% yield by the addition of an equivalent amount of sodium hydroxide to the solution after removing a small amount of undissolved solid (SI Figure S13). The proper regeneration of pristine HKUST-1 was confirmed by IR spectroscopy, PXRD, and N₂ sorption studies (SI Figures S14–S16). The PXRD pattern and IR spectrum of regenerated HKUST-1 are the same as those of Basolite C300, and the porosity of the regenerated HKUST-1 is comparable to that of Basolite C300.

■ CONCLUSION

Herein, we have demonstrated simple and efficient protocols for the regeneration of MOF-5 and HKUST-1 using acid–base treatment. Pristine MOF can be completely recovered simply by dissolving a deteriorated sample in a strong acid. The MOF is regenerated by adjusting the solution pH via either *in situ* base formation or *ex situ* base addition. The recovered yields of MOF-5 and HKUST-1 from deteriorated samples are comparable to the reported yields of as-synthesized MOF-5 and HKUST-1. Whereas the regeneration of MOF-5 is possible only via the *in situ* base formation procedure due to the instability of MOF-5 in water, HKUST-1 can be recovered via both *in situ* base formation in an amide base solvent and *ex situ* base addition in aqueous solution. Both regeneration protocols are environmentally benign, because the deteriorated MOFs can be recycled in high yields. In addition, the protocols are cost-effective, because the expensive ligands can be recycled. The *ex situ* base addition procedure can be carried out under ambient conditions in a cheap and environmentally friendly ethanol/water solvent without using the expensive amide-base solvent needed for *in situ* base formation. In addition, the *ex situ* base addition protocol is suitable for large-scale batch recycling owing to its simple procedure, which involves the dissolution of MOFs in strong acid and subsequent pH adjustment by the addition of strong base and short reaction time.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.cgd.5b01218](https://doi.org/10.1021/acs.cgd.5b01218).

IR spectra, SEM images, PXRD data, and N₂ isotherms of MOFs (PDF)

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Notes

The authors declare no competing financial interest.

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