

Supplementary information

Rationally Designed Amino-Borane Complex in Metal Organic Framework: A Novel Reusable Hydrogen Storage and Size-Selective Reduction Material

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1. Synthesis methods

1.1 Materials

Diethyl ether was purchased in HPLC grade from Aldrich and dried using a solvent purification system (LC Technology SP-1) before usage. All other solvents and chemicals were used as received without further purification.

1.2 Synthetic procedures

1.2.1 Synthesis of UiO-66-NH₂ framework. The UiO-66-NH₂ framework was synthesized according to the published procedure¹ with slight modification. In a typical reaction, 2-aminoterephthalic acid (0.6 mmol) and ZrOCl₂ (0.6 mmol) in 9 ml of DMF and 6 ml of acetic acid were placed in a sealed autoclave and heated to 120 °C for 30 hours. The obtained microcrystalline yellow powder was collected by centrifugation, washed with ~10 ml of DMF to remove the residual terephthalic acid precursor, and then soaked in ~15 ml of methanol for a total of 3 days during which the methanol was refreshed every 10 hours. Finally, the solvent-free UiO-66-NH₂ powder was obtained by heating under vacuum for 24 hours at 150 °C. The nominal formula of UiO-66-NH₂ is Zr₂₄O₁₂₀C₁₉₂H₉₆N₂₄, which has a molecular weight of 6848.1 g/mol.

1.2.2 Synthesis of UiO-66-NH₂-(BH₃)_x (UiOAB). UiO-66-NH₂ was activated by heating at 150 °C under vacuum for 24 hours and refilled with Ar. After cooling with dry ice and acetone for 10 minutes, a 0.2 M solution of borane-dimethyl sulfide (BH₃-Me₂S) in diethyl ether (Et₂O) was slowly added via syringe. The molar ratio of BH₃-Me₂S to UiO-66-NH₂ was 4:1. The mixture was stirred and allowed to warm to room temperature in 5 hours. Then, the solvent was removed under vacuum. A dry yellow solid referred to as UiOAB was obtained and used directly for further analysis.

1.2.3 Synthesis of UiO-66-NH₂-Re. The as-synthesized UiOAB was heated to 90 °C under vacuum for 24 hours to mimic complete dehydrogenation and then soaked in methanol for 3 days during which the methanol was refreshed every 8 hours. Next, the powder was collected by filtration and dried under vacuum at 120 °C for 24 hours to yield UiO-66-NH₂-Re.

1.2.4 Reduction of aldehyde compounds with UiOAB. For a typical procedure, 0.05 mmol of the aldehyde substrate was dissolved in 1 ml of the solvent at a specific temperature, and then, 30 mg of UiOAB (equivalent to 0.1 mmol BH₃ based on a 4.55 wt% borane loading rate) was added to the solution. GC-MS was used to analyze the products using toluene as the internal reference.

2. Methods of characterization

The powder X-ray diffraction (PXRD) were performed on a Bruker D8 Advance X-ray diffractometer with Cu-Kα radiation using a voltage of 40 kV, current of 40 mA, and step size of 0.01° at 0.2 second/step. The uptake of borane was calculated based on the abundance of boron in UiOAB measured by a Varian inductively coupled plasma optical emission spectrometer (ICP-OES). The ¹³C and ¹¹B NMR data were collected using a Bruker 400M MAS system with its internal reference. The rotation frequency was set to 10 kHz for B and 5 kHz for C. Fourier transform infrared spectroscopy (FTIR) was performed on a Nicolet

6700 Smart FTIR spectrometer ranging from 4000 cm^{-1} to 400 cm^{-1} . Thermogravimetric analysis coupled with quadrupole mass spectrometry (TGA-QMS) was used to investigate the thermo dehydrogenation behavior using a heating rate of 1 $^{\circ}\text{C}/\text{min}$ from 50 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$ and Argon flowing rate of 20 ml/min. The nitrogen adsorption/desorption isotherms were measured at 77 K using a Micromeritics ASAP@2420 gas sorption system. Scanning electron microscopy (SEM) was performed on a Quanta 200 FEG system.

Table S1. ICP-OES analysis of Zr and B in UiO-66-NH₂ and UiOAB

| UiO-66-NH ₂ | UiOAB | |
|------------------------|--------|-------|
| Zr wt% | Zr wt% | B wt% |
| 30.97 | 23.96 | 4.55 |

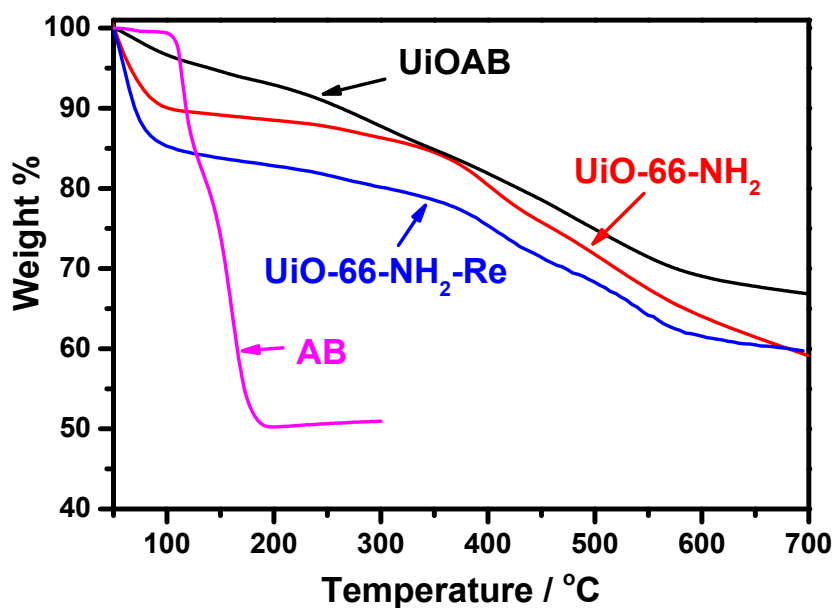


Fig. S1. TGA curve of UiO-66-NH₂ (red), UiOAB (black), UiO-66-NH₂-Re (blue) and neat AB (purple). The sample was heated at 5 $^{\circ}\text{C}/\text{min}$ and purged with argon at 20 ml/min.

3. List of literature results

Table S2 listed the hydrogen release performance of ammonia-borane loaded in different MOF structures reported in literature. The hydrogen loading rate was calculated based on the information provided in the literature. None of these reports discussed the reusability of the host materials.

Table S2. Reported hydrogen release performance of ammonia-borane loaded in different MOF systems.

| Materials | Release T ($^{\circ}\text{C}$) | H ₂ loading rate (wt%) | Pollutant release | Ref. |
|----------------------------------|----------------------------------|-----------------------------------|-------------------|-----------|
| MIL-NH ₂ -101 (Cr) | ~ 73 | 5.6 | Y | 2 |
| JUC-32-Y(Y) | ~ 84 | 0.5 | N | 3 |
| MOF-5 (Zn) | ~ 84 | 0.8 | Y | 4 |
| MIL-NHCOCH ₃ -101(Cr) | ~ 85 | 5.3 | Y | 2 |
| ZIF-8 (Zn) | ~ 85 | 2.7 | Y | 5 |
| MOF-74 (Mg) | ~ 100 | 1.8 | N | 6 |
| MOF-74 (Zn) | ~ 100 | 1.3 | N | 7 |
| MIL-53 (Fe) | ~ 110 | 0.9 | Y | 8 |
| UIOAB | ~ 78 | 2.2 | N | This work |

Y = Detectable, N = Not detectable.

4. Reference

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