Supporting Information for

Improved Hydrogen Release from Hydrolysis of Ammonia–Borane Milling with MOF-74

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Experimental Section

1. Chemicals

Ammonia–Borane (AB) and 2,5-dihydroxyterephthalic acid (DHTA) were purchased from Sigma-Aldrich with no further purification.

2. Preparation of the MOF-74

Co-MOF-74 (Co$_2$C$_8$H$_2$O$_6$) was prepared following the published literature$^1$. Briefly, 1 g of DHTA and 3 g of Co(NO$_3$)$_2$·6H$_2$O were dissolved in 140 mL DMF, 140 mL ethanol, and 140 mL water with sonication. The solution was sealed in 100 mL autoclaves and heated to 100 °C for 3 days. After cooling to room temperature, the resultant product was filtered and washed with methanol. The solid product was immersed in methanol to exchange guest molecules for three times in three days. And then the filtered product was evacuated to 200 °C for 5 hours to dry and kept in argon filled glove box. Ni-MOF-74 (Ni$_2$C$_8$H$_2$O$_6$) was prepared following the same procedure.

3. Ammonia–Borane Milling with MOF-74 (AB-MOF)

In glove box, 900 mg of AB and 100 mg of MOF-74 were added into a ball milling tank and sealed. The tank was operated in a ball mill for 2 hours (30 min very time with 30 min pause). After milling, homogenized mixture of AB and MOF-74 (AB-MOF) was get and kept in glove box (avoiding H$_2$O).

4. Hydrolysis

100 mg AB-MOF was added into a two-neck flask and sealed by two valves. Then, 1 mL H$_2$O was injected from one valve and stirred at room temperature. Meanwhile, the other valve was opened to monitor hydrogen evolution by graduated cylinder with the draining method. An oil bath could be used to keep the reaction at different temperatures.

After the complete hydrolysis of AB-MOF, 90 mg pure AB was added to the system to test the reusability of MOF-74. And this experiment could be done severe times by adding AB into the solution.
5. Characterizations

Powder X-ray diffraction (PXRD) data were performed on Rigaku MIniflex diffractometer with Co Kα radiation. Measuring 2θ range is from 4 ° to 60 ° at the scan rate of 1.2 ° min\(^{-1}\). The voltage and the current were set to be 40 kV and 40 mA, respectively. The Transform Infrared Spectroscopy (FTIR) was collected (4000-400 cm\(^{-1}\) region) on a Nicolet 6700 FTIR spectrometer. N\(_2\) sorption isotherms measurements were performed on a Micro Meritics Tristar Surface Area and Pore Size Analyzer at the temperature of 77 K.

Results Section

Figure S1. (a) XRD patterns of synthesized MOF-74 (red line) and simulated XRD patterns of MOF-74 (black line); (b) TEM image of MOF-74.
Figure S2. Nitrogen adsorption-desorption isotherms of MOF-74 and Pore distribution of MOF-74 (inset).

Figure S3. FTIR patterns of AB (black line), MOF-74 (red line), milling sample AB-MOF (blue line), AB-MOF treated at 200 °C (green line, remove AB by thermolysis to get the patterns of MOF), AB treated at 200 °C (purple line, the end products have no effect to analyze the MOF patterns), and the light blue lines marked the characteristic absorption peaks of MOF-74.

Figure S4. Hydrogen generation from the hydrolysis of AB-NiMOF (90 mg AB milling with 10mg Ni-MOF74, in 1.0 mL H2O, which has no initiating process and faster rate of hydrogen release) at 298 K.