Electronic Supplementary Information

Discovery of Low-Temperature Fe_2O_3 Reduction Route to Fe with Carbon

Bo Huang[*,a,b], *Yuhan Liu*[a] *and Zhe Tan*[a]

[a]Institute of Chemical Engineering and Technology, Xi'an Jiaotong University, Innovation Harbour, Xi-xian New District, Xi'an 712000, China

[b]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

*Corresponding author: bohuang@xjtu.edu.cn.

Experimental details

Synthesis of Needle-like Fe-MOF-74

$FeCl_2$ anhydrous (2.20 g) and 1,4-dihydroxyterephthalic acid (H_4dhtp, 1.42 g) were dissolved in 500 ml of deoxidized N,N-dimethylformamide (DMF) inside glovebox. The solution was kept at 120 ºC for 5 days protected by Ar atmosphere. The product was washed with deoxidized DMF for 3 times, and soaked in deoxidized methanol for 3 times during 3 days. The sample was dried at 60 ºC under vacuum to obtain the as-synthesized sample. It was activated at 140 ºC under vacuum, and stored in glovebox for further use (Fe-MOF-74 is highly air-sensitive).

X-ray Powder Diffraction (XRPD) and Capillary XRPD

The crystal structures of MOFs and their thermal decomposition products were investigated by XRPD analyses using a Bruker D8 Advance diffractometer (Cu $K\alpha$ radiation).

The crystal structures were investigated by capillary XRPD analyses measured a Bruker D8 Advance diffractometer under capillary mode. The XRPD patterns of the samples sealed in a glass capillary was measured *in situ* with Cu $K\alpha$ radiation source.

Transmission Electron Microscopy (TEM)

TEM images were captured using Talos F200X operated at 200 kV accelerating voltage.

Thermal Gravimetric Analysis

Thermal gravimetric analysis was performed with Bruker TG-DTA 2000SA under N_2 gas flow at 100 ml min^{-1}. The temperature range was from room temperature to 800 ºC at an accelerating rate of 5 ºC min^{-1}.

Thermal Treatments

Thermal treatments on Fe-MOF-74 were carried out with BEL-Prep (up to 430 ºC) and quartz tube furnace under vacuum. All the samples were purged with high purity N_2 after treatment.

Procedure for Rietveld Refinement

The Rietveld refinement has been performed by using TOPAS 3.0 (Bruker AXS). For the profile refinement, FP function was used. The refinement by the structural models shown in Table S1 provided the best fit to the XRPD pattern.

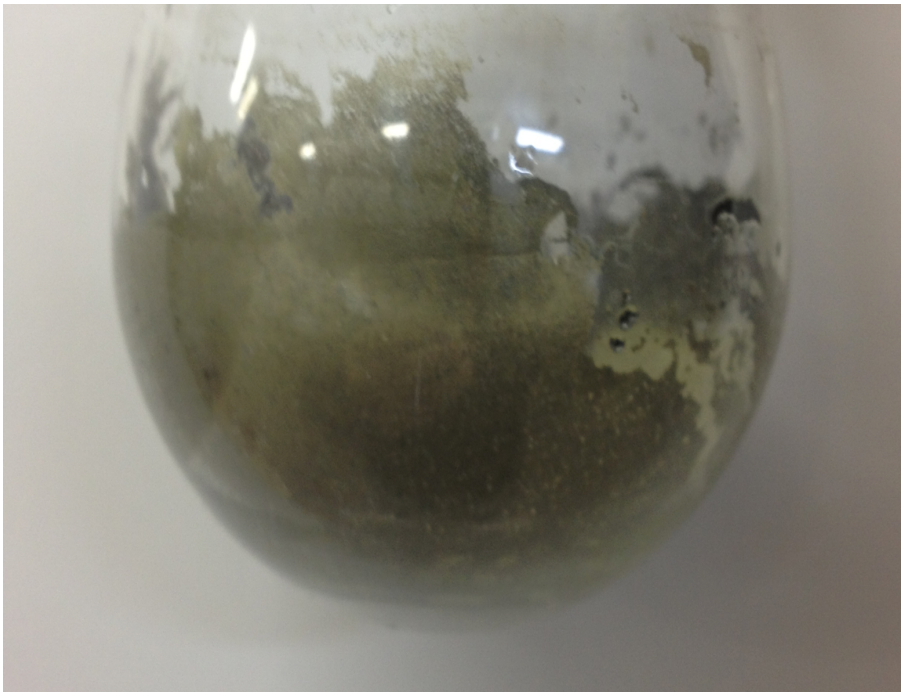

Fig. S1. Photo of the as-synthesized Fe-MOF-74.

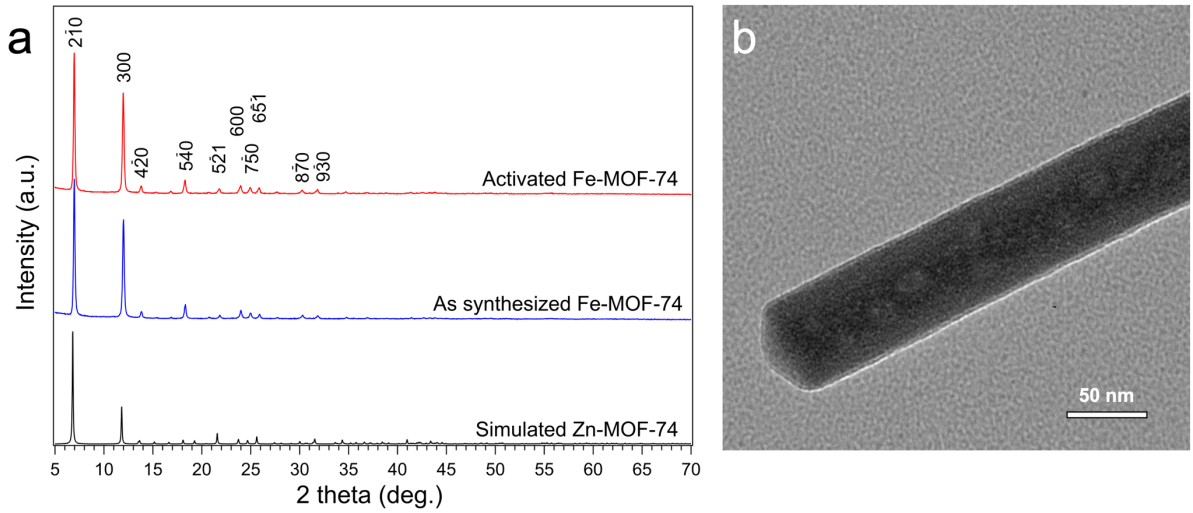

Fig. S2. (a) XRPD patterns of as-synthesized and activated Fe-MOF-74 sealed in capillary at 303 K. The simulated XRPD pattern of Zn-MOF-74 is also displayed. The radiation source was Cu Kα. (b) TEM image of the needle-like Fe-MOF-74.

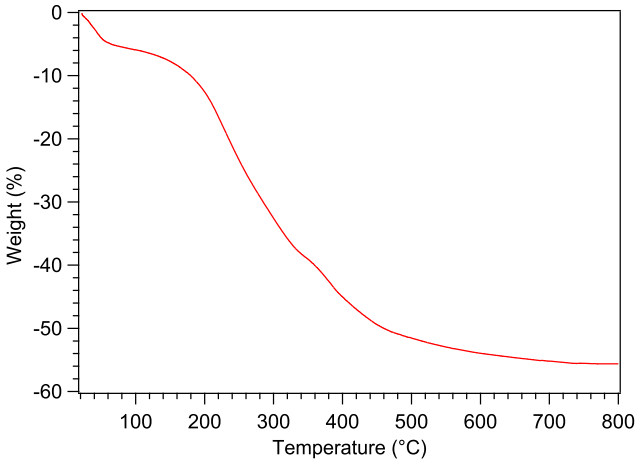

Fig. S3. Thermal gravimetric curve of the as-synthesized Fe-MOF-74.

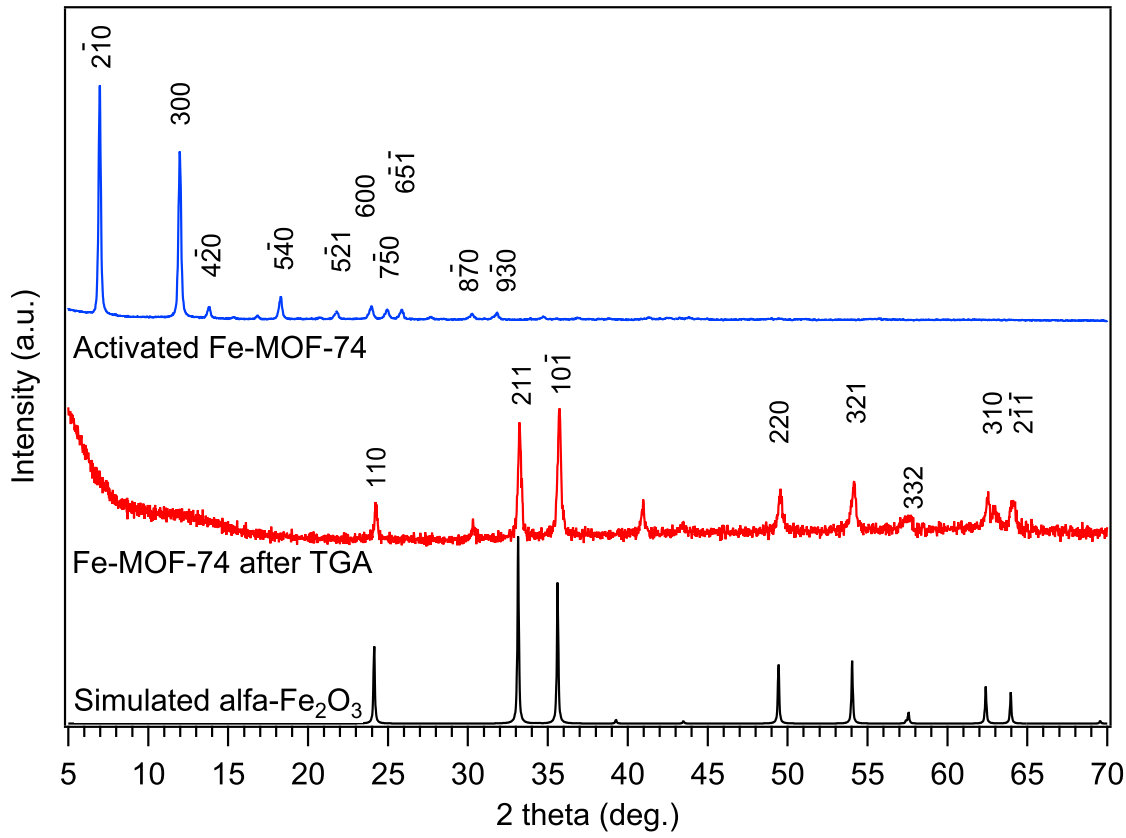

Fig. S4. XRPD patterns of Fe-MOF-74 after TGA at 303 K. The XRPD pattern of activated Fe-MOF-74 and simulated pattern of $\boldsymbol{\alpha}$-Fe_2O_3 are also displayed. The radiation source was Cu $K\boldsymbol{\alpha}$.

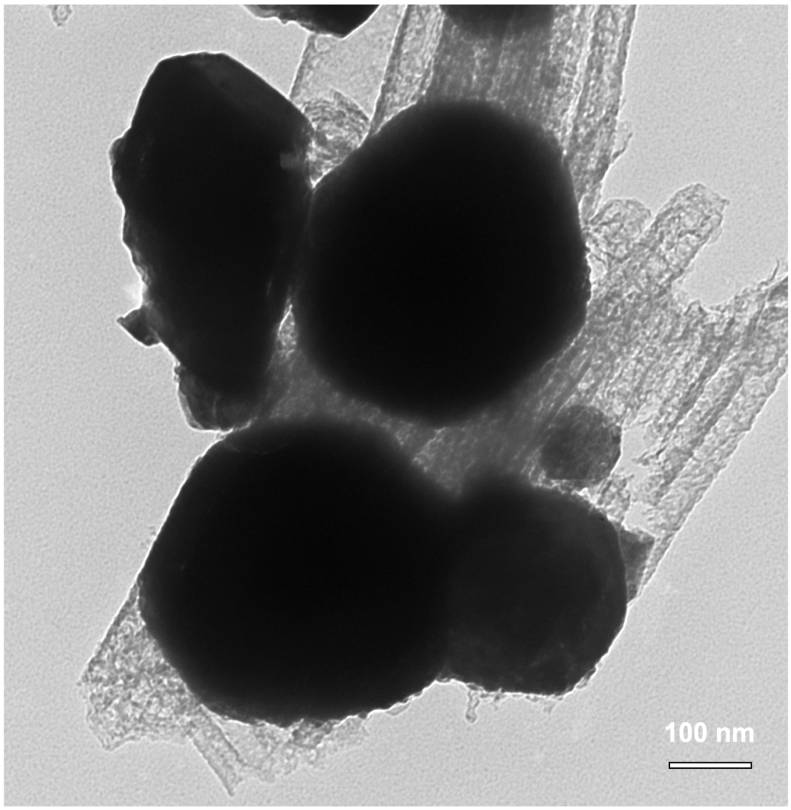

Fig. S5. TEM image of the Fe-MOF-74 thermally treated under vacuum at 700 ºC for 24 h.

Table S1 Structural parameters for $\boldsymbol{\alpha}$-Fe and $\boldsymbol{\gamma}$-Fe_2O_3

T = 303 K, GOF = 1.77

(a) $\boldsymbol{\alpha}$-Fe component, space group**:** *Im*-3*m*

Atom	***x , y, z***	**Occupancy**
Fe	0, 0, 0	1

(b) $\boldsymbol{\gamma}$-Fe_2O_3 component, space group**:** *Fd*-3*m*

Atom	***x , y, z***	**Occupancy**
Fe^{3+}	1/8, 1/8, 1/8	1
Fe^{3+}	1/2, 1/2, 1/2	1
O^{2-}	1/4, 1/4, 1/4	1