Electronic Supplementary Information

Catalytic Nickel Nanoparticles Embedded in a Mesoporous Metal-Organic Framework

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Preparation of Ni@MesMOF-1

Three steps were employed to embed Ni nanoparticles inside MesMOF-1 crystals as follows. MesMOF-1 was prepared by the published procedure (Y. K. Park, et al., *Angew. Chem. Int. Ed.* **2007**, *46*, 8230–8233). The as-prepared MesMOF-1 crystals were washed with neat *N*,*N*-dimethylacetamide and MeOH, and immersed in neat MeOH for 2 days. The solvent was removed under vacuum at room temperature for 1 day, yielding porous material.

- Step 1) Inclusion of evacuated MesMOF-1 with nickelocene by sublimation:

Approximately 30 mg of MesMOF-1 was transferred to a 10 mL vial, which was inserted into a 100 mL round bottom flask containing nickelocene (100 mg). The flask was evacuated with a dynamic 20 mTorr vacuum pressure at room temperature. The flask was sealed and heated to 85 °C in a drying oven. In this manner, three samples were prepared by different heating time; 1, 2 and 3 h. After the sublimation the crystal color became dark violet.

- Step 2) Hydrogenation of included nickelocene in MesMOF-1:

After Step 1, the sample was placed into a 50 mL round bottom flask which is connected to a Schlenk line. Hydrogen gas was supplied with maintaining slightly higher than atmospheric pressure into the flask, and discharged via a bubbler. The flask was heated at 95 °C for 5 h. The hydrogenation of nickelocene was confirmed by ^{1}H-NMR signals of cyclopentane which was produced by the reduction of the cyclopentadineyl ligand in the nickelocene.

- Step 3) Washing out cyclopentane and un-reacted nickelocene with MeOH:

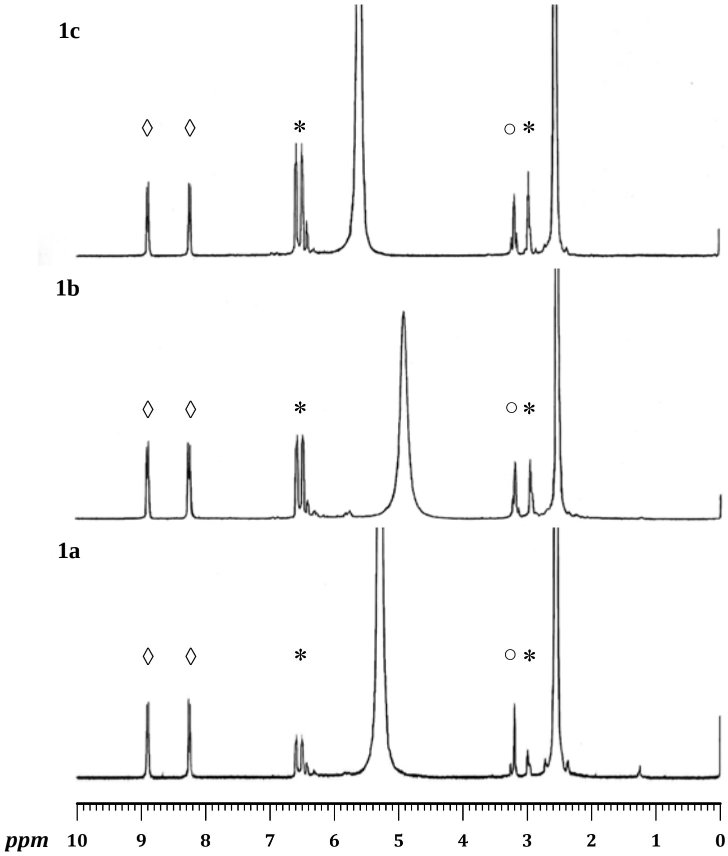
After Step 2, the sample was immersed into a neat MeOH for 5 days to dissolve out pentane. Finally the sample was evacuated under vacuum to produce Ni@MesMOF-**1a**, -**1b**, or -**1c**.

- ICP-AES analysis:

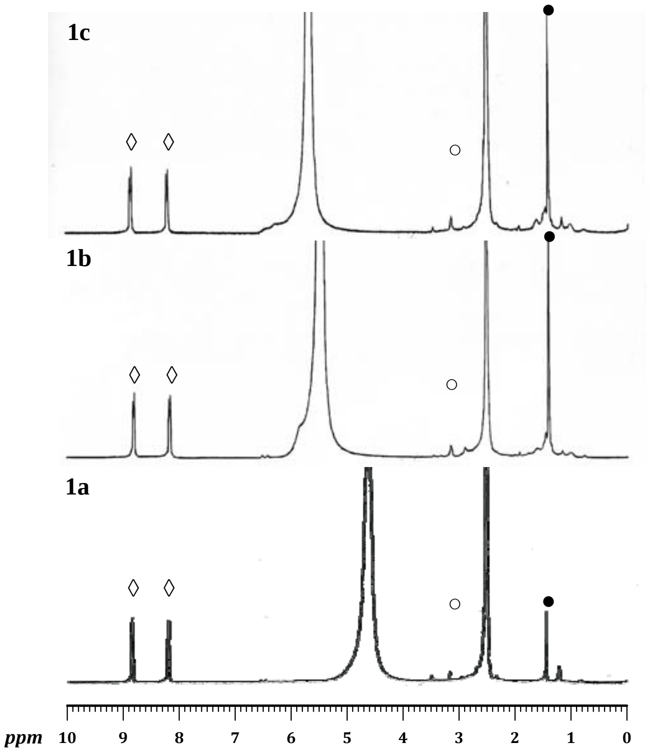
Sample	Ni (ppm)	Tb (ppm)	Ni/Tb (mol ratio)	No. of Ni atoms per f.u.
1a	304.8	308.6	2.674	Ni 42.8
1b	443.6	267.7	4.487	Ni 71.8
1c	596.2	308.1	5.240	Ni 83.8

Fig. S1 ^{1}H-NMR spectra of samples obtained after (a) Step 1, (b) Step 2, and (c) Step 3. (a) Nickelocene gives two sets of signals when it is dissolved in a DCl/dmso-d_6 solution due to the conversion of cyclopentadineyl ligands to cyclopentadiene. Dissolved sample produces signals corresponding to the building block ligand (◊), cyclopentadiene (*), and MeOH(○) that was coordinated to Tb ions in MesMOF-1. (b) After reduction by $H_2(g)$, it was found that cyclopentadiene became cyclopentane (●) while the framework ligand (TATB) was intact. (c) Captured cyclopentane in the pore could be dissolved out when the crystal was immersed in MeOH.

(a)



(b)



(c)

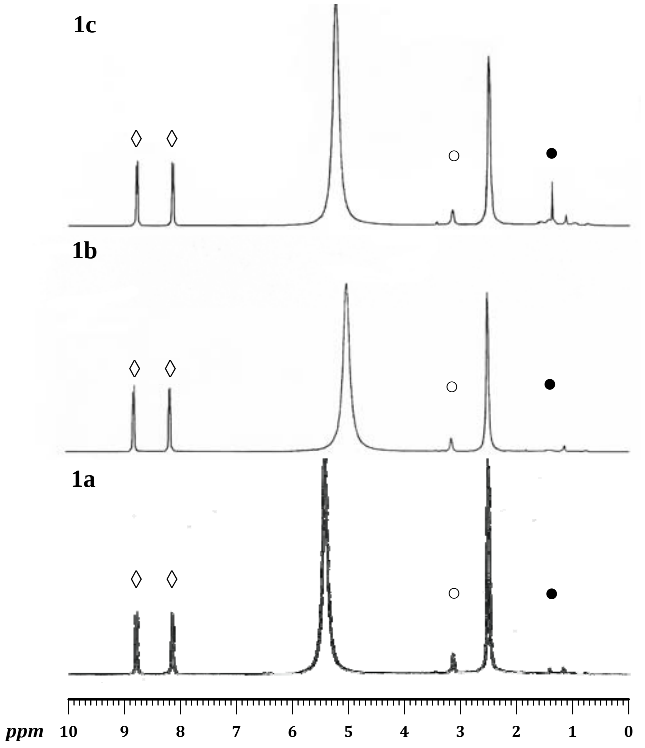


Fig. S2 TGA curves of Ni@MesMOF-**1a**, **1b**, and **1c**. TGA measurements were performed with a TGA-S1000 (Scinco) under an ambient atmosphere. The temperature was increased at a rate of 5°C/min from 25 to 700 °C.

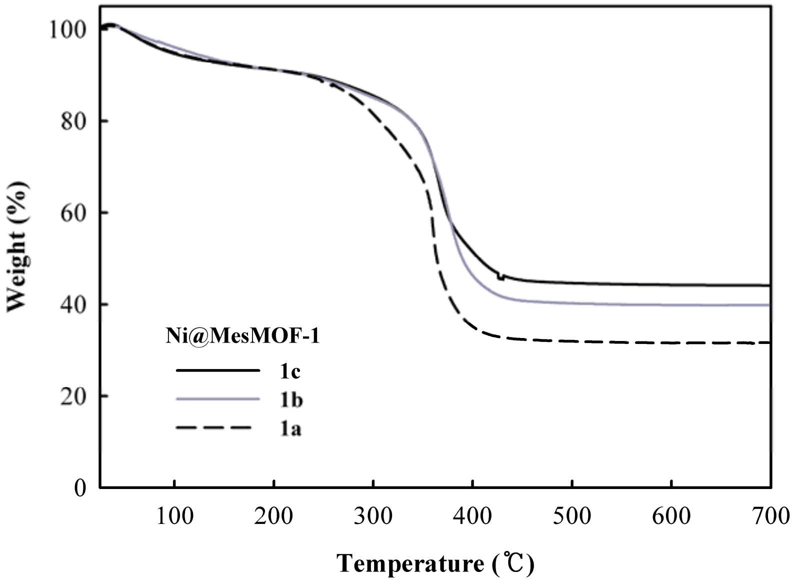


Fig. S3 XRD pattern of Ni@MesMOF-**1c** residue after heating at 700 °C on a TGA apparatus. Both Tb_2O_3 (●) and NiO (○) diffractions are observed.

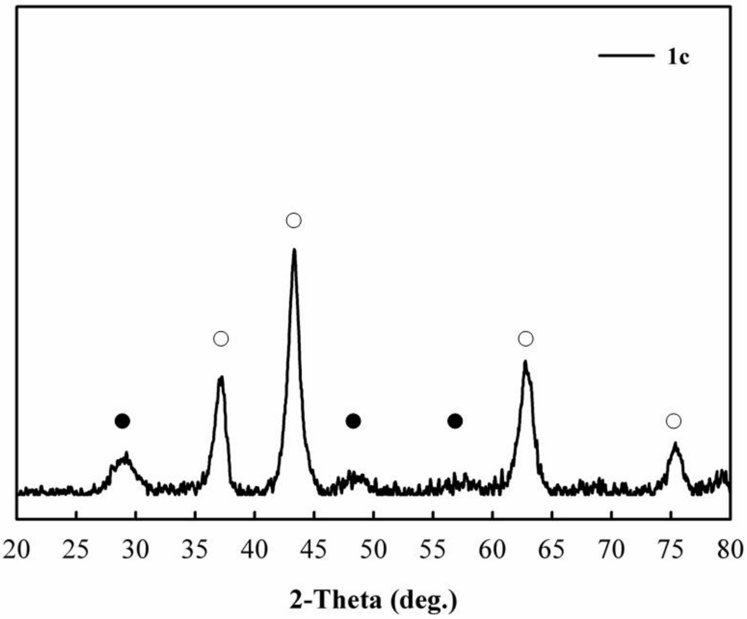


Fig. S4 XRD patterns of Ni@MesMOF-**1a**, **1b**, and **1c** measured with a Rigaku MiniFlex (Cu K_α = 1.5418 Å). Based on Scherrer's equation, the size of Ni nanoparticle in **1c** was estimated to be 4.5 nm, which is greater than the inner diameter of S cage but almost to the same as the L cage. However, this estimation cannot be a judgment for predicting the particle size because other complex factors need to be considered for the reliable estimation (Corain, B.; Jerabek, K.; Centomo, P.; Canton, P. *Angew. Chem. Int. Ed*. **2004**, *43*, 959–962.).

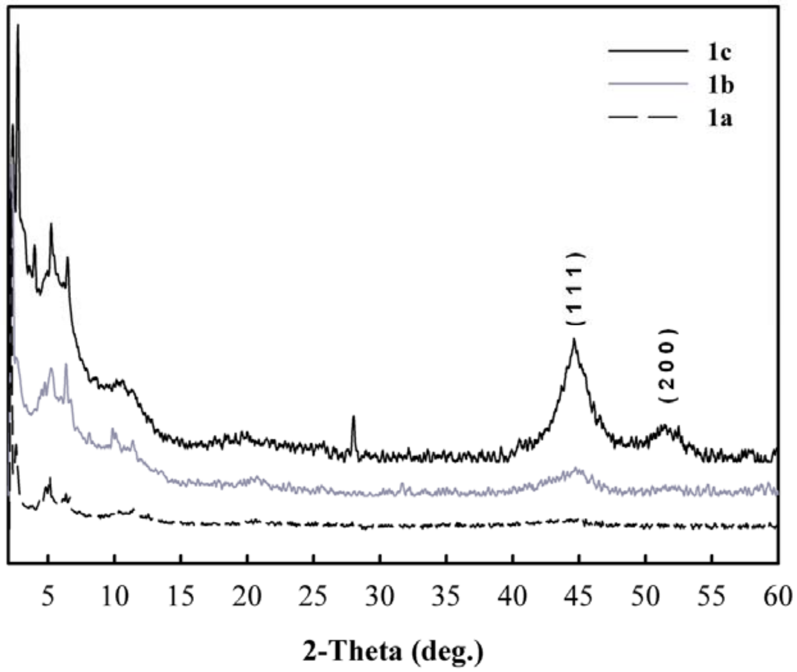


Fig. S5 TEM images of MesMOF-1 obtained on a FE-TEM (JEOL, JEM-2100F, 200 kV) with a 50 nm scale bar.

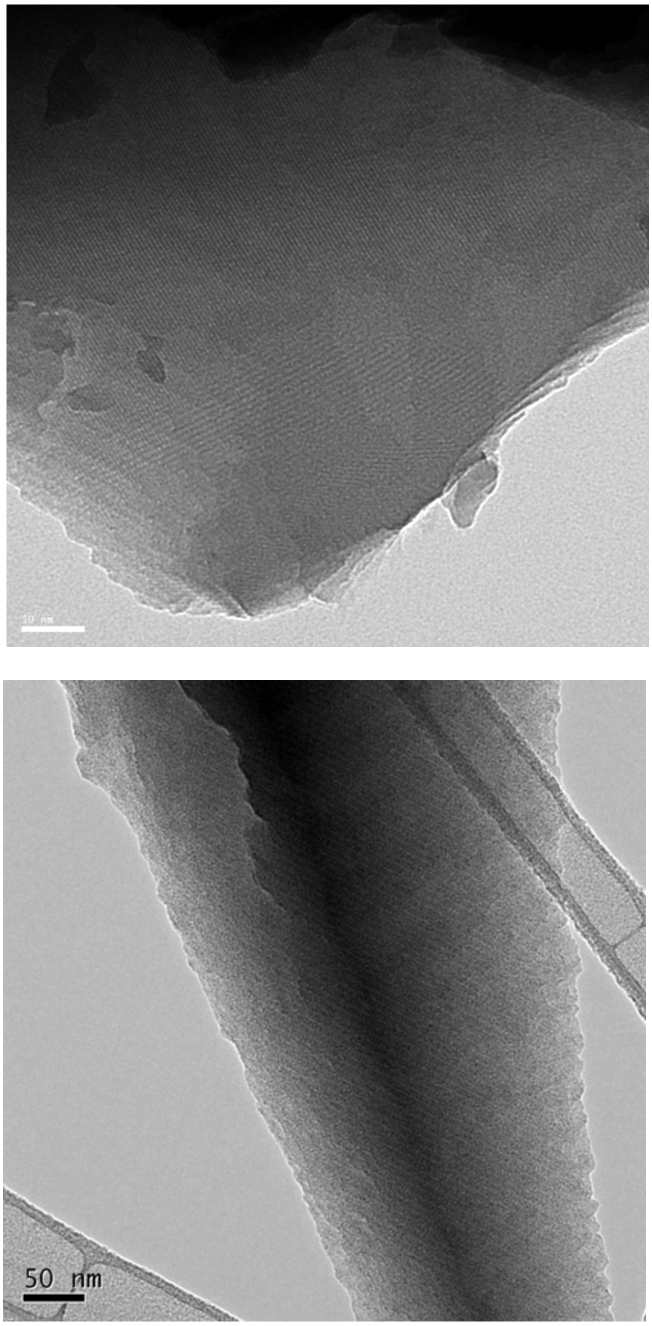


Fig. S6 TEM images of Ni@MesMOF-**1c** obtained on a FE-TEM (JEOL, JEM-2100F, 200 kV) with (top) a 50 nm scale bar, and (bottom) a 20 nm scale bar.

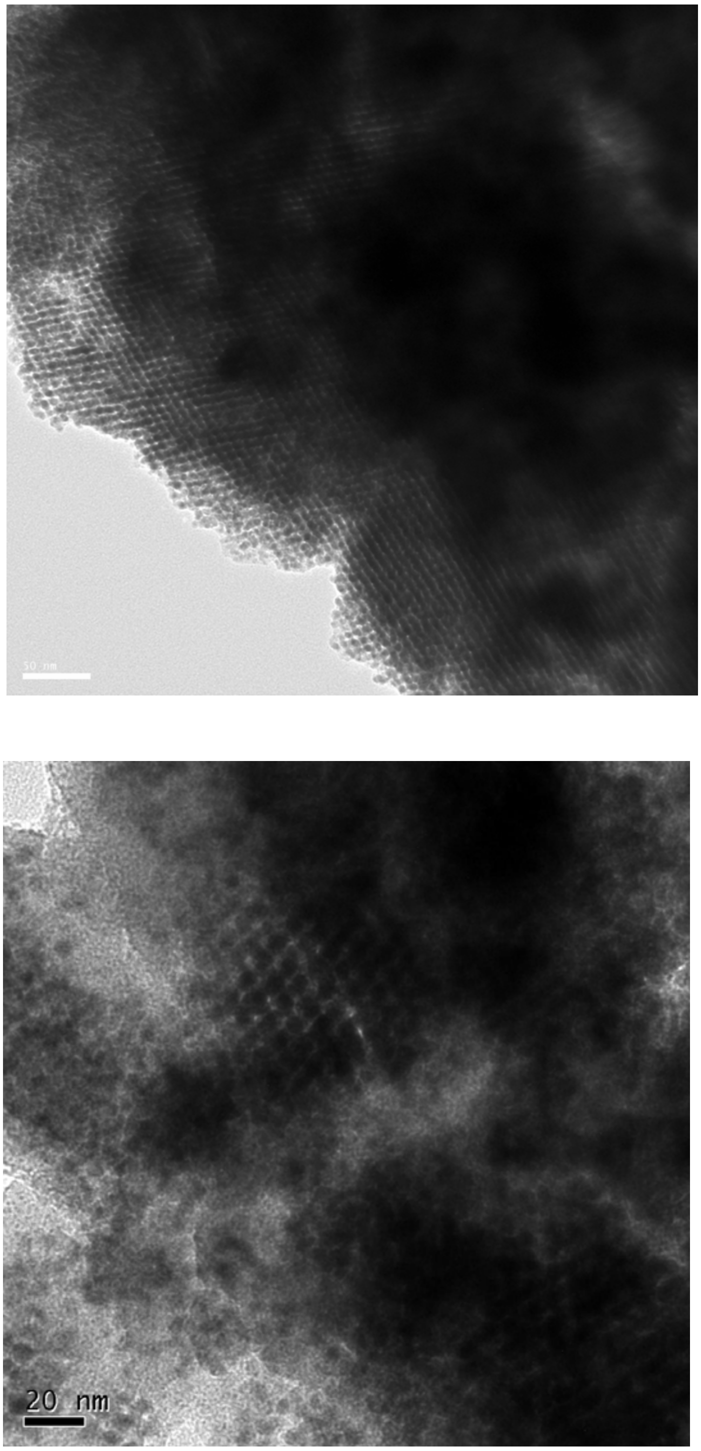


Fig S7 SEM images for **1c** taken at (a) the surface and (b) inner part of the sample. EDS spectra for the each part are shown in (c) and (d). The size of the sample was too large to capture images for the boundaries of the crystal.

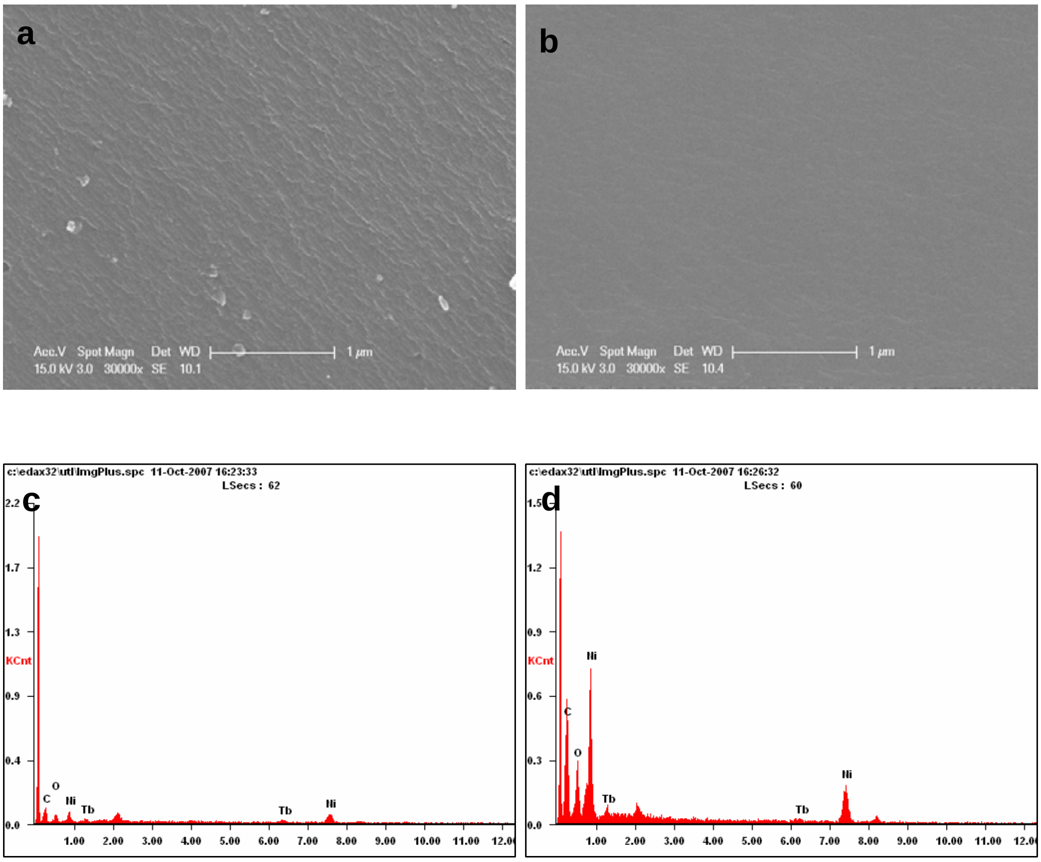
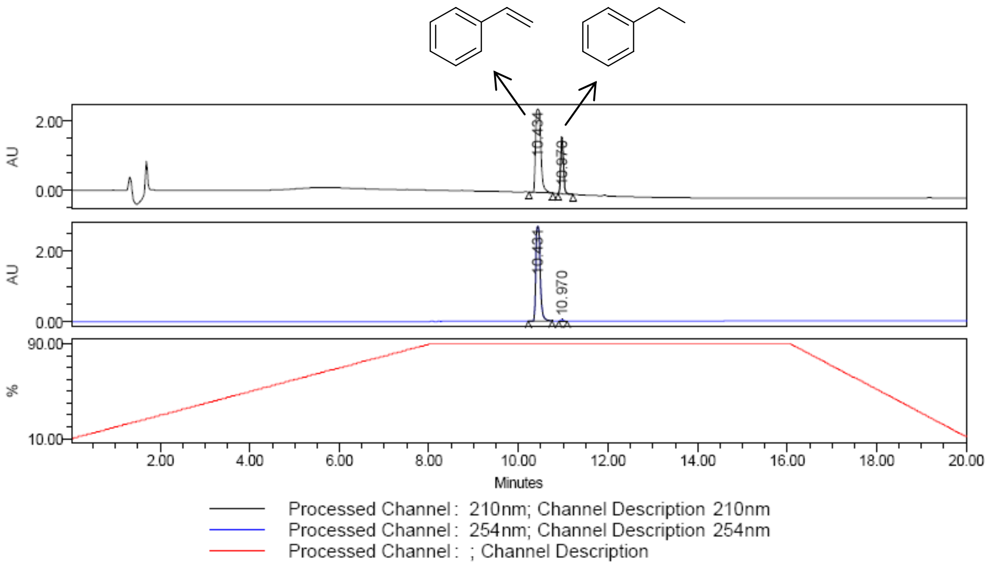
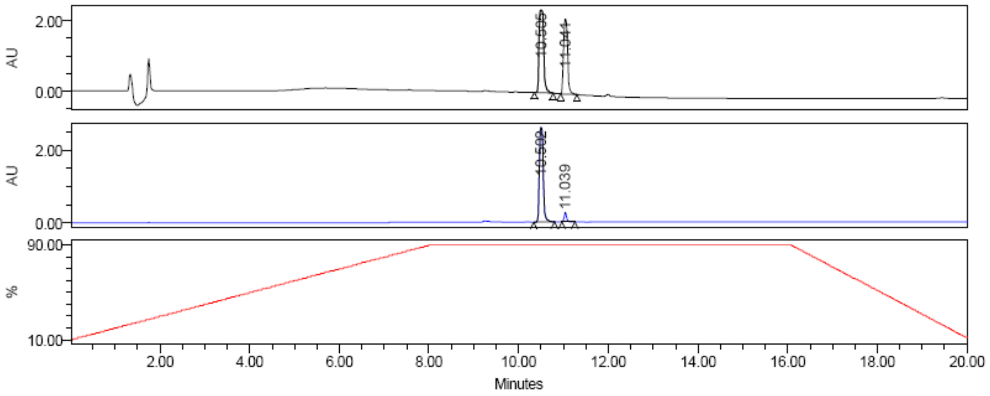


Fig. S8 HPLC chromatograms monitored for the hydrogenation reaction of styrene to ethylbenzene in MeOH. HPLC condition: Waters Symmetry® C_{18} (3.9 mm diameter x 150 mm); eluent A, H_2O with 1% (v/v) TFA; eluent B, CH_3CN with 1% (v/v) TFA; flow rate 1 mL/min.

reaction time: 20 min



reaction time: 1 hr 45 min



reaction time: 4 hr

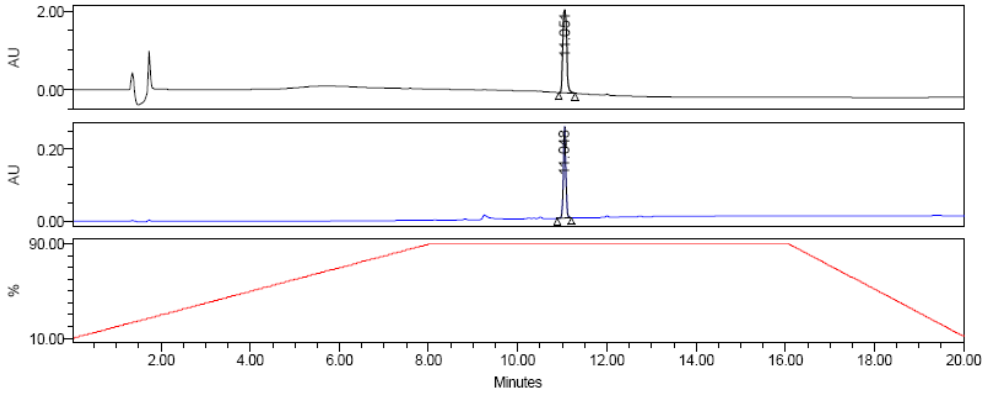


Fig. S9 ^{1}H-NMR spectra for the products collected after hydrogenolysis reactions of nitrobenzene to aniline in MeOH catalyzed by (a) Ni@MesMOF-**1a**, (b) Ni@MesMOF-**1c**, and (c) Raney-Ni, respectively. The spectrum for pure aniline is shown in (d) for comparison.

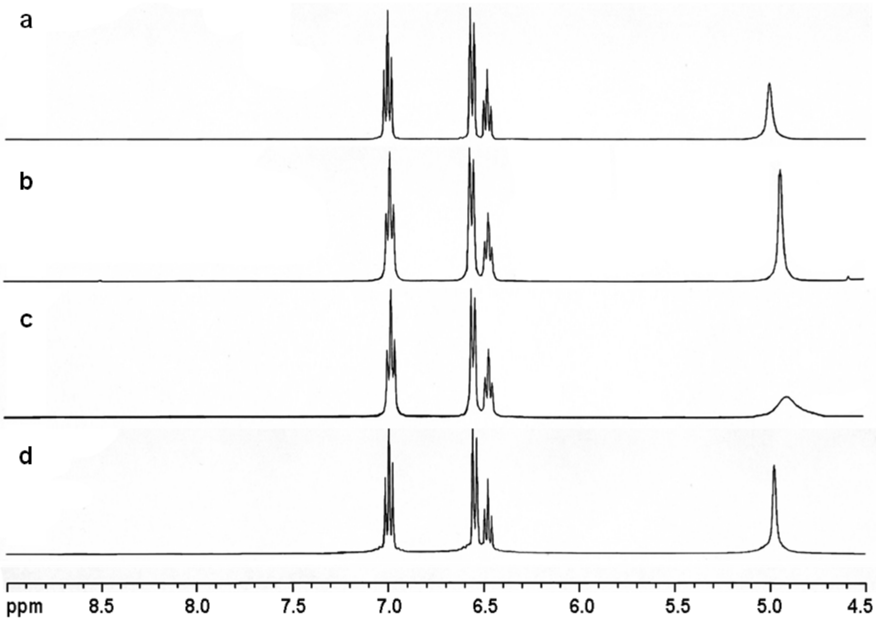


Fig. S10 ^{1}H-NMR spectra for the products collected after hydrogenolysis reactions of nitrobenzene to aniline in H_2O/THF catalyzed by (a) Ni@MesMOF-**1a**, (b) Ni@MesMOF-**1c**, and (c) Raney-Ni, respectively. The spectra for pure (d) azobenzene and (e) aniline are shown for comparison. Observed species are (a) azoxybenzene, azobenzene, and aniline, (b) azoxybenzene and aniline, and (c) azoxybenzene and azobenzene **after 24 h reaction time**.

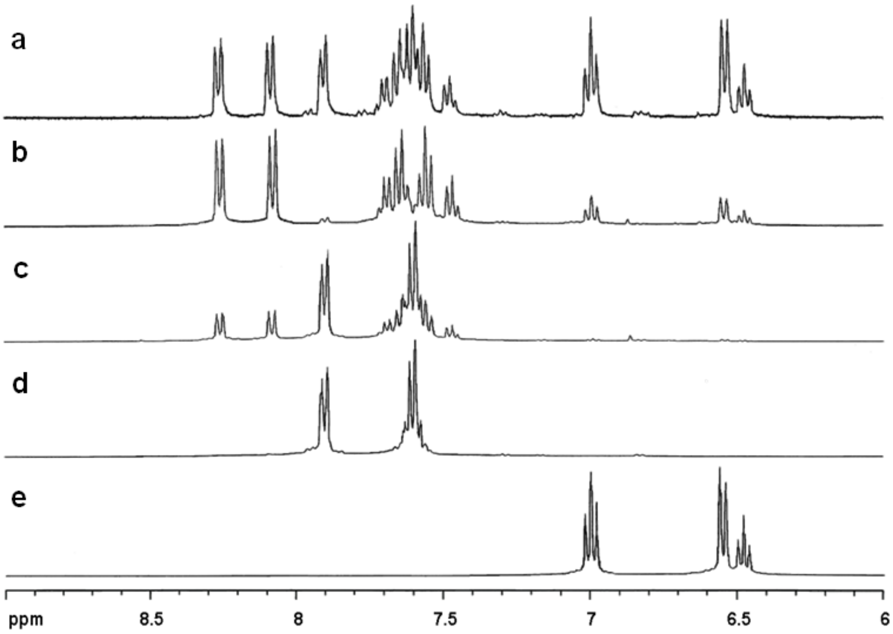


Fig. S11 ^{1}H-NMR spectra for the products collected after hydrogenolysis reactions of nitrobenzene to aniline in H_2O/THF catalyzed by (a) Ni@MesMOF-**1a**, and (b) Ni@MesMOF-**1c**. Observed species are (a) azoxybenzene, azobenzene, aniline, and nitrobenzene, and (b) azoxybenzene, azobenzne, and aniline **after 6 h reaction time**.

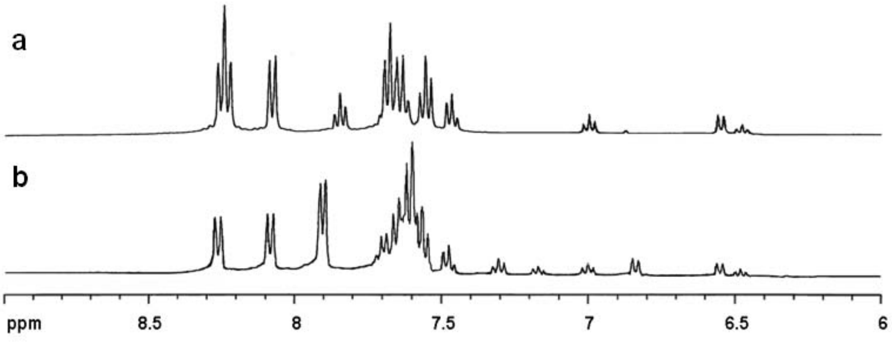


Fig. S12 ^{1}H-NMR spectrum for the products collected after stirring nitrobenzene and $NaBH_4$ in a MeOH-filtrate for 15 min at room temperature. The filtrate was obtained by removing **1c** after stirring it in a pure MeOH for 12 h at room temperature. The main signals are from nitrobenzene, and the trace signals may be from azobenzene and azoxybenzene.