

Electronic Supplementary Information

Low-cost CuNi@MIL-101 as an excellent catalyst toward cascade reaction: integration of ammonia borane dehydrogenation with nitroarene hydrogenation

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1. Materials and Instrumentation.

All chemicals were purchased from commercial sources and used without further treatment: chromium(III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sigma-Aldrich, 99%), 1,4-benzene dicarboxylic acid (TCI, >99%), aqueous HF (Aladdin Industrial Inc., 40%), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was purchased from Energy Chemical Corp., ammonia borane (NH_3BH_3 , Sigma-Aldrich, 90%), anhydrous *n*-hexane (Sinopharm Chemical Reagent Co., Ltd., $\geq 97\%$), methanol (CH_3OH , Sinopharm Chemical Reagent Co., Ltd., >99%), nitrobenzene (Sinopharm Chemical Reagent Co., Ltd., CP), nitromethane (Aladdin Industrial Inc., AR), nitroethane (Aladdin Industrial Inc., 99%), 2-nitrotoluene (Aladdin Industrial Inc., 99%), 3-nitrotoluene (Aladdin Industrial Inc., 98%), 4-nitrotoluene (Aladdin Industrial Inc., 99%), 4-nitrobenzyl alcohol (Energy Chemical, 98%), 4-nitrophenol (Aladdin Industrial Inc., AR), 2-nitroaniline (Aladdin Industrial Inc., 99%), 3-nitroaniline (Aladdin Industrial Inc., 98%), 4-nitroaniline (Aladdin Industrial Inc., AR), 1,3-dinitrobenzene (Aladdin Industrial Inc., CP) and 4-fluoronitrobenzene (Aladdin Industrial Inc., 98%). De-ionized water with the specific resistance of $18.25 \text{ M}\Omega \cdot \text{cm}$ was obtained by reversed osmosis followed by ion-exchange and filtration (Cleaned Water Treatment Co., Ltd., Hefei). The transmission electron microscopy (TEM) and high resolution TEM (HRTEM) were acquired on JEOL-2010 with an electron acceleration energy of 200 kV. Powder X-ray diffraction patterns (PXRD) were carried out on a Japan Rigaku SmartLabTM rotation anode X-ray diffractometer equipped with graphite monochromatized Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). Nitrogen sorption isotherms were

measured by using an automatic volumetric adsorption equipment (Micromeritics ASAP 2020). Prior to nitrogen adsorption/desorption measurement, the samples were dried for 12 h at 433 K under vacuum. The contents of Cu and Ni in CuNi@MIL-101 were quantified by an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES). The catalytic reaction products were analyzed and identified by gas chromatography (GC, Shimadzu 2010 Plus with a 0.25 mm × 30 m Rtx-5 capillary column).

2. Catalyst Preparation.

Preparation of MIL-101: MIL-101 was synthesized and purified according to the reported procedures.^{S1} A typical synthesis involves a solution containing $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (4.33 g, 10.8 mmol), 1,4-benzene dicarboxylic acid (1.8 g, 10.8 mmol), de-ionized water (52 mL), aqueous HF (0.3 mL, 1.5 mmol). The mixture was introduced into a Teflon-lined autoclave and heated for 8 h at 473 K in an oven under static condition. To remove organic species trapped within the pores, the purification treatment was performed using the boiling water for 24 h. After filtering with the glass filter, the resulting solid was purified twice in ethanol at reflux temperature for 24 h. The crystalline MIL-101 product was filtered and washed with hot ethanol. To obtain the pure crystals, the as-synthesized MIL-101 was further activated by the aqueous NH_4F solutions. The sample was finally dried at 433 K for 12 h under dynamic vacuum prior to the further use.

Preparation of $\text{Cu}^{2+}/\text{Ni}^{2+}@$ MIL-101: Typically, 200 mg of activated MIL-101 was suspended in hydrophobic solvent of dry *n*-hexane (40 mL). The mixture was sonicated for 30 min to make sample evenly dispersed in the hexane. To which 0.30 mL aqueous solution of 15.1 mg $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 39.6 mg $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was pumped dropwise into the flask under continuous vigorous stirring and the mixture were stirred for another 3 h. After stirring, the green powder settled down to the bottom of the flask samples, which can be separated through the dumping of supernatant fluid and was simply dried in air at room temperature. The synthesized sample was further dried overnight at 433 K under dynamic vacuum.

Preparation of CuNi@MIL-101: A certain amount of Cu²⁺/Ni²⁺@MIL-101 was stirred in 10 mL mixture solution of methanol and water ($v : v = 2 : 3$) with 30 mg ammonia borane and 0.1 mmol nitroarene. The Cu²⁺ and Ni²⁺ were rapidly reduced *in situ* during the hydrolytic/methanolytic dehydrogenation of ammonia borane to give CuNi@MIL-101.

Preparation of Cu²⁺Ni²⁺/MIL-101 by wet impregnation method: An aqueous solution of an appropriate volume containing 4.1 mg Cu(NO₃)₂·3H₂O and 13.1 mg Ni(NO₃)₂·6H₂O was added dropwise to 100 mg of MIL-101 with vigorous agitation by a glass rod. The slurry was stirred for over 30 min and then dried at 60 °C for 12 h under vacuum.

Preparation of CuNi/MIL-101 for activity comparison: A certain amount of Cu²⁺Ni²⁺/MIL-101 was stirred in 10 mL mixture solution of methanol and water ($v : v = 2 : 3$) with 30 mg ammonia borane and 0.1 mmol nitrobenzene. The Cu²⁺ and Ni²⁺ were rapidly reduced *in situ* during the hydrolytic/methanolytic dehydrogenation of ammonia borane to give CuNi/MIL-101.

3. Catalytic Activity Characterization.

Catalytic performance evaluation for CuNi@MIL-101 toward ammonia borane

dehydrogenation reaction only: In general, a mixture of 33.5 mg $\text{Cu}^{2+}/\text{Ni}^{2+}@MIL-101$, 4 mL methanol and 6 mL de-ionized water was placed in a two-necked round-bottomed flask (25 mL) under magnetic stirring. A gas burette filled with water was connected to the reaction flask to measure the volume of hydrogen evolved. To reduce the divalent metal Cu^{2+} and Ni^{2+} , 10 mg NH_3BH_3 was added into the flask prior to the catalytic reaction. To catalyze the ammonia borane dehydrogenation, NH_3BH_3 (20 mg) was introduced to the above mixture solution in the presence or absence of nitroarene (0.1 mmol). And then, the volume of the evolved hydrogen gas was immediately monitored by recording the displacement of water in the gas burette. The reaction was completed when there was no more gas generated.

Catalytic performance evaluation for CuNi@MIL-101 in the cascade reaction:

Typically, a mixture of 33.5 mg $\text{Cu}^{2+}/\text{Ni}^{2+}@MIL-101$, 30 mg NH_3BH_3 was placed in a two-necked round-bottomed flask (25 mL). The reaction started when the solution contained 4 mL methanol, 6 mL de-ionized water and 0.1 mmol nitroarene was added into the flask under magnetic stirring. For the catalytic recycling/durability experiments, the same amount of NH_3BH_3 (30 mg) and nitroarene (0.1 mmol) were added into the flask to initiate the reaction. After the completion of the reaction with different time lengths, 30 μL of the resultant mixture was taken to a mixed solvent with 1 mL H_2O and 1 mL ethyl acetate. Upon the adequate shaking, the above mixture was allowed to be centrifuged and the reaction product was extracted to the

upper layer of ethyl acetate. Then, 600 μL of sample in the upper solution was detected by GC.

Table S1 Catalytic performance comparison between CuNi@MIL-101 and previously reported Ni-based catalysts toward the nitrobenzene hydrogenation.

Entry	Catalyst	Solvent	Reducing agent	TOF (h ⁻¹)	Ref.
1	0.26%Ni@0.47%Pd/AC	EtOAc	H ₂	15	S2
2	[Ni ₃ (Ni-HTCPCP) ₂ (μ ₂ -H ₂ O) ₂ (H ₂ O) ₄ (DMF) ₂]·2DMF	EtOH	NaBH ₄	33.3	S3
3	Fe-Ni (10 mol%)	MeOH	NaBH ₄	17.1	S4
4	NiFe ₂ O ₄ -DA-Pd	MeOH	NH ₃ BH ₃	6.6	S5
5	CuNi@MIL-101	MeOH/H ₂ O	NH ₃ BH ₃	99.2	This work

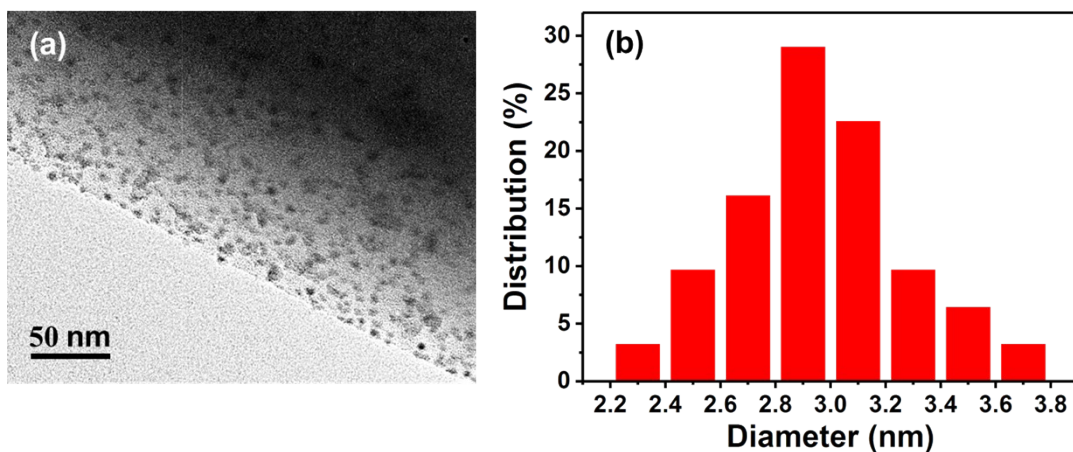


Fig. S1 (a) TEM image of CuNi@MIL-101 and (b) the size distribution for CuNi NPs.

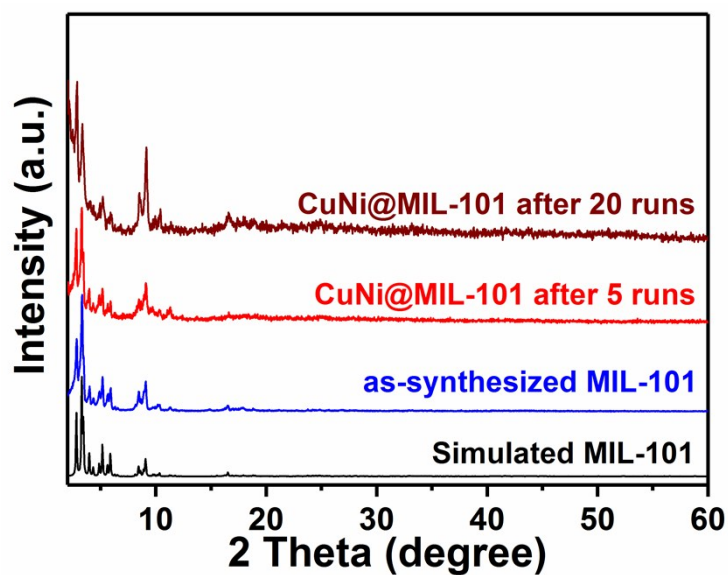


Fig. S2 PXRD patterns of simulated MIL-101, as-synthesized MIL-101 and CuNi@MIL-101 after cycle of dehydrogenation of ammonia borane and hydrogenation of nitroarenes.

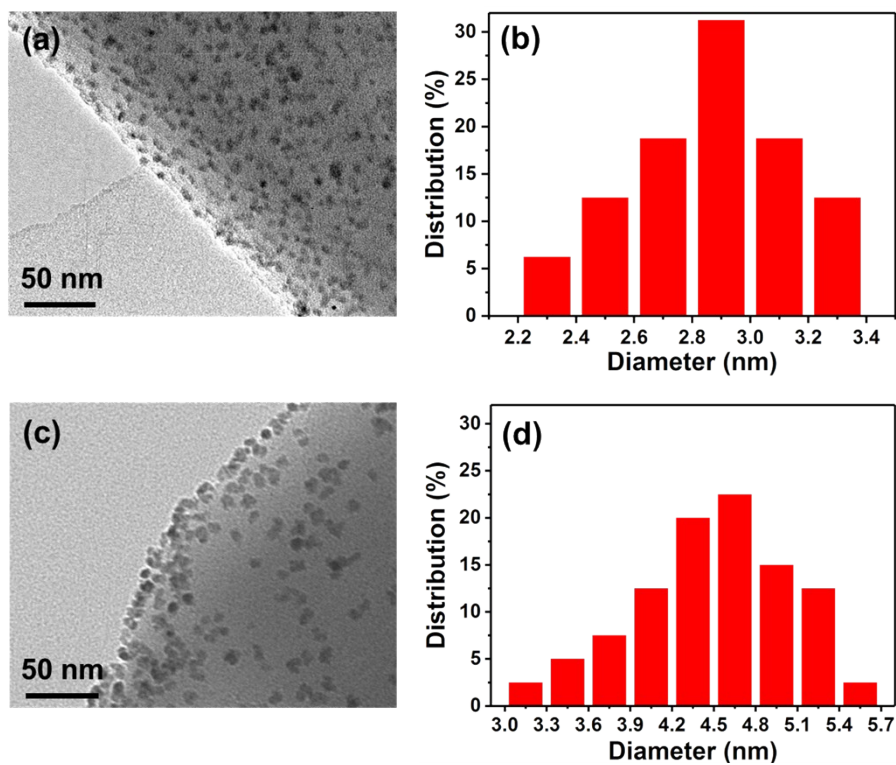


Fig. S3 (a) TEM image for CuNi@MIL-101 after 5 catalytic runs and (b) the size distribution for CuNi NPs; (c) TEM image for CuNi@MIL-101 after 20 catalytic runs (d) the size distribution for CuNi NPs.

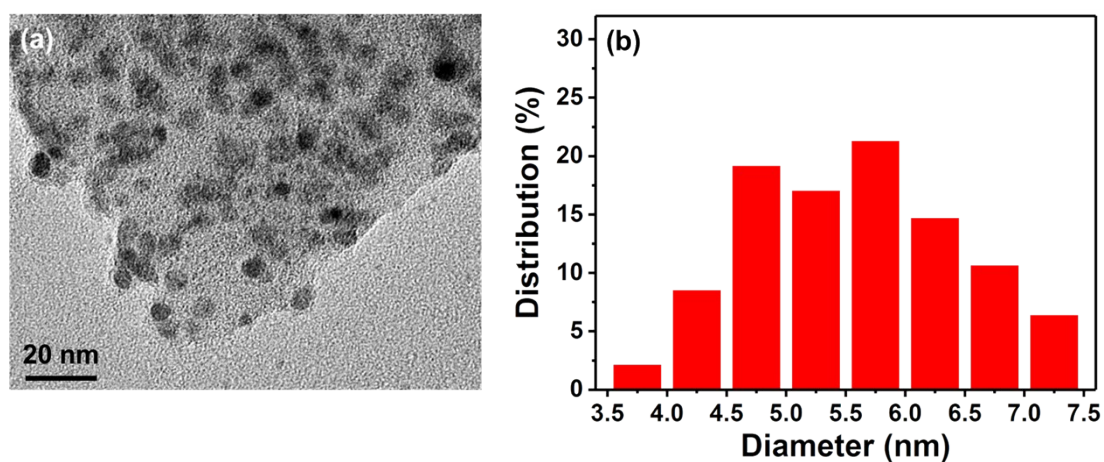


Fig. S4 (a) TEM image for CuNi/MIL-101 prepared by the wet impregnation method and (b) the size distribution for CuNi NPs.

References

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