Ru@UiO-66(Ce) Catalyzed Acceptorless Dehydrogenation of

Primary Amines to Nitriles: The Roles of Lewis Acid-base pairs on

the Reaction

Guo-Ping Lu,^{a,b*+} Xinxin Li,^{a+} Lixiang Zhong,^b Shuzhou Li^b, Fei Chen^c

^a School of Chemical Engineering, Nanjing University of Science & Technology, Xiaolingwei 200,

Nanjing 210094, P. R. China

^b School of Materials Science & Engineering, Nanyang Technological University, 50 Nanyang

Avenue, Singapore 639798

^c Nanjing Institute of Environmental Sciences, Ministry of Ecology and Environment, Nanjing,

210042, China

*Corresponding authors: glu@njust.edu.cn

⁺These authors are contributed equally to this paper.

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1 General Considerations

All chemical reagents are obtained from commercial suppliers and used without further purification. GC-MS was performed on an ISQ Trace 1300 in the electron ionization (EI) mode. GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m \times 320 μ m \times 0.25 μ m, carrier gas: H₂, FID detection. All NMR spectra were recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz and 126 MHz in CDCl₃, respectively, and chemical shifts were reported in ppm. The crystal structure of the synthesized catalysts were recorded by Xray diffraction (XRD) using a D8ADVANCED X-ray diffractometer, employing a scanning rate of 0.1°s⁻¹. Scanning electron microscope (SEM) images were taken using a Hitachi S-4800 apparatus on a sample powder previously dried and sputter-coated with a thin layer of gold. Transmission electron microscopy (TEM) images were taken using a PHILIPS Tecnai 12 microscope operating at 120 kv. High Resolution Transmission electron microscopy (HRTEM) was performed on Philips-FEI Tecnai G2 F20 operating at 300kv. X-ray photoelectron spectroscopy (XPS) were performed on a ESCALAB 250Xi spectrometer, using a Al Ka X-ray source (1350 eV of photons). Inductively coupled plasma mass spectrometry (ICP-MS) was analyzed on Optima 7300 DV. Raman spectra were recorded on Aramis with a wavelength of 532 nm. Temperature-programmed desorption (TPD) of NH₃ and CO₂-TPD were conducted on a Quantachrome TPRWin v3.52 instrument. The samples were pretreated in He flow at 200 °C with a rate of 15 mL/min for 30min and cooled to 50 °C, and then swept in CO₂ (NH₃) flow with a rate of 15 mL/min for 40 min. After treatment in He flow for 50 min to remove physical adsorption, the sample were raised at a heating rate of 10 °C/min to 500 °C, the signals were monitored by a TCD detector. BET surface areas were performed with N₂ adsorption/desorption isotherms at 77 K on a Micromeritics ASAP Tri-star II 3020 instrument. Before measurements, the samples were degassed at 150 $^{\circ}$ C for 12 h. The generated H₂ gas was detected by a gas chromatograph (Shimadzu GC-2014; Molecular sieve 5A, TCD detector, Ar carrier gas) using a syringe. The Raman spectra were obtained using confocal Raman spectroscopy (inVia-Reflex) employing 785 nm radiation (3 mW).

2 Preparation of catalysts

MOFs-encapsulated Ru NPs catalysts were prepared by follow procedures. 500 mg support dissolves into 25 mL of water, ultrasonic treatment after metal precursor RuCl₃ (10.3 mg, 0.05 mmol, content of Ru: 5 mg) was added into the mixture, and lysine aqueous solution (0.53 M, 5 mL) was added with vigorous stirring for 4 h at low temperature (< 5°C). Later, NaBH₄ aqueous solution (0.50 M, 3 mL) was added into suspension liquid dropwise while keeping the temperature below 10 °C. The mixture was continually stirred for 2 h to ensure that metal precursor was completely reduced.

Then stop stirring and add acetone (5 mL) keeping for 24 hours. Finally, the catalyst was centrifuged, washed with water and ethanol for three times and dried at 100 °C under vacuum.

The preparation of UiO-66(Ce)-encapsulated bimetallic catalysts (denoted as $Ru_1M_n@UiO-66(Ce)$, Pd/M = 1/n, M = Ni and Nb) is the same with MOFsencapsulated Ru NPs catalysts, except the step of adding metal precursors. For $Ru_1M_n@UiO-66(Ce)$, two kinds of metal precursors were introduced: $RuCl_3$ (10.3 mg, 0.05 mmol, content of Ru: 5 mg), another metal salt (0.05*n mmol).

Ru NPs was prepared according to the reported literature.^[1] RuCl₃ (12.3 mg) and PVP (55.5 mg) were dissolved in ethylene glycol (10 mL) at room temperature. The mixture was heated at 170 °C for 6 h. The color of the solution changed from dark red to dark brown. An aliquot of 10 mL Ru NPs solution was purified by anhydrous acetone for three times and then dispersed to1 mL of ultrapure water.

3 Preparation of MOFs

3.1 Preparation of UiO-66(Ce)

UiO-66(Ce) was synthesized according to the previous literature.^[2] 1,4benzendicarboxylic acid (H₂BDC, 708 mg) was introduced into the round bottom. After the addition of DMF (24 mL), cerium (IV) ammonium nitrate (8mL, 0.5333 M) aqueous solution was added. The glass reactor was sealed and stirred for 30 min at 100 °C. The suspension liquid was allowed to cool to room temperature, light yellow precipitate was centrifuged and collected. The solid was washed and centrifuged with DMF (40 mL) and acetone (40 mL) four times. Finally, the obtained sample was soaked in methanol (50 mL) to remove redundant solvents and further activated for 24 h at 100 °C at a low pressure to obtain the activated sample.

3.2 Preparation of UiO-66(Zr)

UiO-66(Zr) was synthesized according to reported method with a slight modification,^[3] ZrCl₄ (0.96 g) and H₂BDC (1.32 g, 0.8 mmol) were dissolved in DMF (160 mL), mixed solution was placed into a 150mL Teflon-lined stainless steel autoclave and ultrasonic treatment for 20min. Following that, mixture was heated at 120°C for 24h. The solid products were collected by centrifugation and washed with DMF (twice) and ethanol (twice). The resulting UiO-66(Zr) samples were dried at 60°C overnight.

3.3 Preparation of MIL-101(Fe)

MIL-101(Fe) was synthesized by a hydrothermal method according to a previously reported procedure.^[4] Typically, FeCl₃·6H₂O (1.35 g, 5.0 mmol) and H₂BDC (0.42 g, 2.5 mmol) were dissolved in DMF (25 mL). Ultrasonic treatment for 15 min to make the solid fully dissolved. Then the mixture was transferred to a Teflon-lined stainless steel autoclave and heated at 110 °C in an oven for 24 h. The dark orange solid products

were separated by centrifugation and purified with DMF and hot ethanol. Afterwards, the purified products were dried at 70 °C for 30 min. Finally, the materials were activated in an oven at 150 °C for 8 h.

3.4 Preparation of MIL-125(Ti)

MIL-125(Ti) was synthesized based on a previously reported procedure.^[5] Briefly, a mixture of DMF (27 mL) and CH₃OH (3 mL) was divided into two parts. Tetrabutyl titanate (1.8 mL) and H₂BDC (1.65 g) were added to each part, respectively. After ultrasonication and dissolution, the two parts were combined in a 50 mL Teflon-lined stainless steel autoclave and heated at 150 °C for 48 h. After the reaction, the resultant precipitate was separated by centrifugation and washed repeatedly with CH₃OH. The obtained powder sample was dried in a vacuum oven at 80 °C for 12 h.

3.5 Preparation of Mg-MOF-74

The synthesis of Mg-MOF-74 was achieved by following a previously reporte with a slight modification.^[6] 2,5-Dihydroxyterephthalic acid (0.37 g, 1.9 mmol) and Mg(NO₃)₂·6H₂O (1.56 g, 6.1 mmol) were dissolved in the mixture of DMF (150 mL), ethanol (10 mL), and water (10 mL) with sonication for 10 min. And then the mixture was transferred to a round bottom. The bottles were tightly sealed and heated at 125 °C for 26 h. The solid products were collected by centrifugation and washed with methanol. Finally, the products were combined to one bottle, immersed in methanol and exchanged into fresh methanol daily for 4 days. Purified products were dried in a vacuum oven.

4 The general procedures for the acceptorless double dehydrogenation

of primary amines

A mixture of primary amine 1 0.2 mmol, Ru@UiO-66(Ce) 1 mol% were added in H_2O (1 mL), which was stirred under atmospheric N₂ at 130 °C for 16 h. After the reaction was completed, the reaction mixture was extracted by EtOAc (2 mL*2). The obtained organic layer was collected and removed in *vacuo* to afford the crude product 2. Further column chromatography on silica gel was required to afford the pure desired products. The catalyst was centrifuged from the reaction mixture after completion of the reaction, washed with methanol and water, dried in a drying oven and then reused in new reaction.

5 XRD results



Figure S1. Powder XRD patterns





Figure S2. The N₂ adsorption/desorption isotherms

Table S1. BET surface areas

Material	Ru@CeO ₂	Ru@UiO-66(Ce)	UiO-66(Ce)
BET surface area (m ² /g)	35	251	919

7 ICP-MS results of Ru@UiO-66(Ce) catalyst

Table S2.	ICP-MS	analysis	of the I	Ru/UiO	-66(Ce)	catalyst
		2				2

Catalyst	Metal	Metal Content (mg/Kg)	wt%
Ru@UiO-66(Ce)	Ru	7964.7	0.80
Ru@UiO-66(Ce) ^a	Ru	7679.6	0.77

^a It was recycled after four runs.

8 XPS results



Figure S3. XPS patterns of (a) high resolution of Fe spectrum of MIL-101(Fe) (b) high resolution of Ti spectrum of MIL-125(Ti) (c) high resolution of Zr spectrum of UiO-66(Zr)

The XPS spectra of catalyst recycled after four runs in the O 1s region are similar with Ru@UiO-66(Ce) (Figure S4a). The peak at the binding energy about 529.9 eV and 513.1 eV arise from the surface lattice oxygen specie (O_L) and defect oxides (O_{DC}) respectively.^[7] Catalyst used for fourth with a lower ratio of O_{DC}/O_L in comparison with fresh catalyst which result in the lower catalytic performance. XPS spectra of Ce 3d was shown in Figure S4b. the peaks of catalyst used for fourth without obvious difference compared with Ru@UiO-66(Ce), but the intensity of Ce³⁺ which was labeled with v' (884.5 eV) and u' (903.0 eV) tend to visibly decrease. Table S3 displays the calculated ratio of O_{DC}/O_L and Ce³⁺/Ce⁴⁺ for the catalysts using integrated intensity (peak area) of each component obtained from deconvolution of XPS spectra.



Figure S4. XPS patterns of (1) Ru@UiO-66(Ce) recycled after four runs and (2) Ru@UiO-66(Ce) (a) O 1s, (b) Ce 3d, (c) C 1s-Ru 3d

Table S3. $O_{DC}\!/O_L$ and $Ce^{3+}\!/Ce^{4+}\!ratios$ of catalysts from XPS spectra.

Sample	O _D /O _L	Ce ³⁺ /Ce ⁴⁺
Ru@UiO-66(Ce)	1.84	0.46
Ru@UiO-66(Ce) ^a	0.95	0.32

^a It was recycled after four runs.

9 SEM images of Ru@UiO-66(Ce) recycled after four runs



(b)



Figure S5. (a), (b) SEM images and (c), (d) TEM images of Ru@UiO-66(Ce) recycled after four

runs



10 Detection and measurement of the produced gas

Figure S6. The GC spectra of (a) pure H₂; (b) air; (c) the gas in the reactor drawn into a syringe for GC detection.

Reaction of dehydrogention of dodecylamine (0.1 mmol) to dodeconitrile was carried out under optimized reaction conditions. After the reaction, the reaction mixture was allowed to cool to room temperature, put a soap bubble at the bottom of the gas burette and then connect the sealed tube with the gas burette by a rubber tube. Turn the plug, gas released from the tube run into the gas burette along the rubber tube, position of the soap bubble will be changed, so we could know the volume of the produced gas by comparing the initial position and final position of the soap bubble. Caution!!! Open the plug of the reaction tube as slowly as possible, the soap bubble will be blown away if the inlet gas is in a high speed. As shown in Figure S7, volume of the evolved gas was measured to be 3 mL, very close to the theoretical value.



Figure S7. Left: Experimental setup; middle: initial position of the soap bubble; right: final position of the soap bubble

11 ¹H NMR, ¹³C NMR spectra and characterization data of nitrile compounds



Dodecanenitrile **2a**,^[8] colorless oil, yield 72%, 52.1 mg. ¹H NMR (500 MHz, CDCl₃) δ 2.38 (t, *J* = 7.1 Hz, 2H), 1.81-1.65 (m, 2H), 1.53-1.43 (m, 2H), 1.32 (d, *J* = 13.7 Hz, 14H), 0.93 (t, *J* = 6.9 Hz, 3H). GC-MS (EI) m/z: 181.



Octanenitrile **2b**,^[9] colorless oil, yield 88%, 44.0 mg. ¹H NMR (500 MHz, CDCl₃) δ 2.32 (t, J = 7.1 Hz, 2H), 1.70 - 1.56 (m, 2H), 1.50 - 1.36 (m, 2H), 1.31 - 1.20 (m, 6H), 0.87 (t, J = 6.9 Hz, 3H). GC-MS (EI) m/z: 125.



Tetradecanenitrile 2c,^[8] colorless oil, yield 60%, 50.2 mg. ¹H NMR (500 MHz, CDCl₃) δ 2.38 (t, J = 7.2 Hz, 2H), 1.77 - 1.65 (m, 2H), 1.56 - 1.42 (m, 2H), 1.32 (d, J = 15.2 Hz, 18H), 0.93 (t, J = 6.9 Hz, 3H).. GC-MS (EI) m/z: 209.



¹H NMR of 2d



Stearonitrile **2d**, colorless crystal, m.p. 40-42 °C, yield 62%, 65.7 mg. ¹H NMR (500 MHz, CDCl₃) δ 2.38 (t, J = 7.1 Hz, 2H), 1.77 - 1.65 (m, 2H), 1.56 - 1.42 (m, 2H), 1.32 (d, J = 16.7 Hz, 26H), 0.93 (t, J = 6.9 Hz, 3H). GC-MS (EI) m/z: 265.



Benzonitrile **2e**,^[9] colorless oil, yield 25%, 10.3 mg. ¹H NMR (500 MHz, CDCl₃) δ 7.73 - 7.67 (m, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H). GC-MS (EI) m/z: 103.



2-Methylbenzonitrile 2f,^[8] colorless oil, yield 53%, 24.8 mg. ¹H NMR (500 MHz, CDCl₃) δ 7.64 (d, J = 7.7 Hz, 1H), 7.53 (t, J = 7.0 Hz, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.32 (dd, J = 9.3, 6.4 Hz, 1H), 2.60 (s, 3H). GC-MS (EI) m/z: 117.



3-Methylbenzonitrile 2g,^[8] colorless oil, yield 90%, 42.1 mg. ¹H NMR (500 MHz, CDCl₃) δ 7.50 (dd, J = 2.0, 1.4 Hz, 2H), 7.45 (d, J = 7.7 Hz, 1H), 7.40 (td, J = 7.8, 4.1 Hz, 1H), 2.43 (s, 3H). GC-MS (EI) m/z: 117.



¹H NMR of 2h



3-Methoxybenzonitrile **2h**,^[10] Brownish yellow oil, yield 68%, 36.2 mg. ¹H NMR (500 MHz, CDCl₃) δ 7.45 - 7.38 (m, 1H), 7.29 (t, *J* = 9.0 Hz, 1H), 7.17 (dd, *J* = 5.9, 2.8 Hz, 2H), 3.88 (s, 3H).GC-MS (EI) m/z: 133.



¹³C NMR of 2i



4-Methylbenzonitrile 2i,^[8] colorless oil, yield 37%, 17.3 mg. ¹H NMR (500 MHz, CDCl₃) δ 7.59 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 2.47 (s, 3H). GC-MS (EI) m/z: 117.



4-Chlorobenzonitrile **2j**,^[8] colorless crystal, m.p. 91-93 °C (lit. 92 °C), yield 64%, 35.1 mg. ¹H NMR (500 MHz, CDCl₃) δ 7.65 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H).. GC-MS (EI) m/z: 137.



¹H NMR of 2k



2-Phenylacetonitrile 2k,^[10] colorless oil, yield 64%, 30.0 mg. ¹H NMR (500 MHz, CDCl₃) δ 7.43 (dd, J = 9.1, 5.8 Hz, 2H), 7.39 (t, J = 6.2 Hz, 3H), 3.79 (s, 2H). GC-MS

Mass: 117

(EI) m/z: 117.





¹H NMR of 2l

cis-9-Octadecenenitrile 2I,^[8] colorless oil, yield 86%, 90.5 mg. ¹H NMR (500 MHz, CDCl₃) δ 5.53 - 5.19 (m, 2H), 2.37 (t, *J* = 7.1 Hz, 2H), 2.08 - 1.83 (m, 4H), 1.69 (dd, *J* = 14.7, 7.3 Hz, 2H), 1.34 (d, *J* = 26.3 Hz, 20H), 0.92 (t, *J* = 6.1 Hz, 3H). GC-MS (EI) m/z: 263.



Quinoline 4 ^[11] colorless oil, yield 75%, 38.7 mg.¹H NMR (500 MHz, CDCl₃) δ 8.95 - 8.84 (m, 1H), 8.12 (dd, *J* = 12.8, 9.1 Hz, 2H), 7.78 (d, *J* = 5.5 Hz, 1H), 7.73 - 7.64 (m, 1H), 7.56 - 7.46 (m, 1H), 7.38 - 7.29 (m, 1H). GC-MS (EI) m/z: 129.

12 Calculation results



Figure S8. The adsorption structures of hydrogen on different oxygen sites of Ru@UiO-66(Ce). Yellow is Ce; red is O; brown is C; silver is Ru; light gray is H.



Figure S9. The adsorption structures of n-propylamine on different Ce sites of Ru@UiO-66(Ce). Yellow is Ce; red is O; brown is C; silver is Ru; light gray is H; light blue is N.

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