## **Supporting Information**

# **Encapsulation of Ultrafine Metal-Oxides Nanoparticles within Mesopores for Biomass-Derived Catalytic Applications**

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### This PDF file includes:

Materials and methods Tables S1 to S5 Figures S1 to S12

#### Experimental

All reagents are of analytical grade and were used without further purification.

#### Synthesis of ZIF-67

In a typical synthesis, 0.73 g of  $Co(NO_3)_2 \cdot 6H_2O$  was dissolved in 15 mL methanol to form a clear solution A. Then, 0.82 g of 2-methylimidazole was dissolved in 15 mL methanol to form a clear solution B. The solutions A and B were mixed together at room temperature and stirred for 24 h. The resulting purple powder was washed with methanol several times and dried under vacuum at 50 °C overnight.

#### Synthesis of Co@KIT-6

In a typical synthesis, a 5 mL methanol solution containing Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.02 g) and KIT-6 (1.0 g) was first prepared and treated with under vacuum to remove the adsorbed air. Then, another 5 mL of freshly prepared methanol solution containing 2-methylimidazole (1.15 g) was added under vigorous stirring. The mixture was further stirred for 24 h under vacuum, followed by centrifugation and washing with methanol for several times. The resultant powder was denoted as ZIF-67@KIT-6. After drying at 50 °C overnight, the ZIF-67@KIT-6 sample was calcined at 250 °C for 3 h with a heating rate of 1 °C min<sup>-1</sup> from room temperature in O<sub>2</sub> atmosphere. The obtained material was denoted as Co@KIT-6.

For comparison, the ZIF-67@KIT-6 samples were subjected to different calcination progresses. The prepared materials were denoted as Co@KIT-6-x, where x indicated the calcination temperatures or heating rates.

#### Synthesis of Cu@KIT-6

In a typical synthesis, a 5 mL methanol solution containing  $Cu(NO_3)_2 \cdot 3H_2O$ (0.73 g) and KIT-6 (1.0 g) was first prepared and treated under vacuum to remove the adsorbed air. Then, another 5 mL of freshly prepared methanol solution containing 1,3,5-benzenetricarboxylate (0.17 g) was added under vigorous stirring. The mixture was further stirred at 80 °C for 20 h under vacuum, followed by centrifugation and washing with methanol for several times. The resultant powder was denoted as HKUST-1@KIT-6. After drying at 50 °C overnight, the HKUST-1@KIT-6 sample was calcined at 250 °C for 3 h with a heating rate of 1 °C min<sup>-1</sup> from room temperature in O<sub>2</sub> atmosphere. The obtained material was denoted as Cu@KIT-6.

#### Synthesis of Fe@KIT-6

In a typical synthesis, a 5 mL *N*,*N*-dimethylformamide solution containing  $FeCl_3 \cdot 6H_2O(0.81 \text{ g})$  and KIT-6 (1.0 g) was first prepared and treated under vacuum to remove the adsorbed air. Then, another 5 mL of freshly prepared *N*,*N*-dimethylformamide solution containing terephthalic acid (0.5 g) was added under vigorous stirring. The mixture was further stirred at 100 °C for 12 h under vacuum, followed by centrifugation and washing with *N*,*N*-dimethylformamide for several times. The resultant powder was denoted as MIL-88b@KIT-6. After drying at 50 °C overnight, the MIL-88b@KIT-6 sample was calcined at 250 °C for 3 h with a heating rate of 1 °C min<sup>-1</sup> from room temperature in O<sub>2</sub> atmosphere. The obtained material was denoted as Fe@KIT-6.

#### Synthesis of Ni@KIT-6

In a typical synthesis, a 5 mL methanol solution containing Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.02 g) and KIT-6 (1.0 g) was first prepared and treated under vacuum to remove the adsorbed air. Then, another 5 mL of freshly prepared methanol solution containing 2-methylimidazole (1.15 g) was added under vigorous stirring. The mixture was further stirred at 140 °C for 12 h under vacuum, followed by centrifugation and washing with methanol for several times. The resultant powder was denoted as Ni-ZIF@KIT-6. After drying at 50 °C overnight, the Ni-ZIF@KIT-6 sample was calcined at 250 °C for 3 h with a heating rate of 1 °C min<sup>-1</sup> from room temperature in O<sub>2</sub> atmosphere. The obtained material was denoted as Ni@KIT-6.

#### Synthesis of KIT-6-blank

In a typical synthesis, a 5 mL methanol solution containing KIT-6 (1.0 g) was prepared and treated with liquid nitrogen under vacuum to remove the adsorbed air. After that, another 5 mL freshly prepared methanol solution containing  $Co(NO_3)_2 \cdot 6H_2O$  (0.73 g) was added under vigorously stirring. The mixture was stirred for 24 h under vacuum followed by centrifugation and washing with methanol for several times, the obtained powder was denoted as KIT-6-blank.

#### Synthesis of Co/KIT-6

Co/KIT-6 was prepared by a wetness impregnation method. In a typical synthesis, a 5 mL methanol solution containing KIT-6 (1.0 g) was prepared. Then, another 5 mL

freshly prepared methanol solution containing  $Co(NO_3)_2 \cdot 6H_2O$  (1.02 g) was added under vigorous stirring. The mixture was further stirred for 24 h followed by centrifugation and drying at 50 °C overnight. Then the pink powder was calcined at 250 °C for 3 h with a heating rate of 1 °C min<sup>-1</sup> from room temperature in O<sub>2</sub> atmosphere. The obtained material was denoted as Co/KIT-6.

#### **Catalyst characterization**

Powder X-ray diffraction (PXRD) patterns of the samples were obtained on a Rigaku diffractometer (D/MAX-IIIA, 3kW) using Cu K $\alpha$  radiation (40 kV, 30 mA,  $\lambda$  = 0.1543 nm). BET surface areas and pore size measurements were performed with N<sub>2</sub> adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2020M instrument. Before measurements, samples were degassed at 100 °C for 12 h. The cobalt contents in the samples were measured quantitatively by atomic absorption spectroscopy (AAS) on a HITACHI Z-2300 instrument. Elemental analysis was performed on an Elementar Vario EL III equipment by weighing samples of 0.2–0.3 mg and packing with aluminum foil for the measurement. Fourier transform infrared spectroscopy (FT-IR) measurements were carried out on a Thermo Fisher iS10 instrument equipped with a liquid nitrogen cooled MCT detector. The magnetic properties of the catalyst were measured on a Quantum Design physical property measurement system (PPMS-9). Thermogravimetric analysis (TG) was carried out on a NETZSCH STA 409 PC/PG under air atmosphere (20 mL·min<sup>-1</sup>).

The size and morphology of materials were studied by scanning electron

microscopy (SEM) and transmission electron microscopy (TEM). SEM was carried out on a Zeiss Merlin instrument. TEM and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were recorded on a JEOL JEM-2010F instrument equipped with EDX analysis (Bruker XFlash 5030T) operated at 200 kV. In order to better analyze the dispersion and the sizes of the cobalt oxide nanoparticles, the samples were embedded in Spurr's resin and cut into ~30 nm thin sections using the ultramicrotome.

XPS measurements were performed in a ultra-high vacuum (UHV) multipurpose surface analysis system (SpecsTM model Germany) operating at pressures  $<10^{-10}$ mbar using a conventional X-ray source (XR-50, Specs, Mg K<sub>alpha</sub>, 1253.6 eV) in a "stop-and-go" mode to reduce potential damage due to sample irradiation. Binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon. Deconvolution curves for the XPS spectra were obtained using software supplied by the spectrometer manufacturer.

#### General procedures for HMF oxidation

In a typical run, HMF (1.0 mmol) and catalyst (metal 1 mol%) were added to  $H_2O$  (3 mL) in the autoclave with magnetic stirrer. After purging the reactor several times with air, the reactor was maintained at 80 °C, 0.1 MPa air for 2 h with a stirring speed of 600 rpm. During the reaction, samples were taken and analyzed by HPLC (Shimazu LC-20A). The first sample was taken when the reaction temperature reached 80 °C. After reaction, the reactor was cooled to room temperature and the catalyst was isolated from the solution by centrifugation, washed with methanol and

reused directly.

The conversion of HMF, selectivity and yield of FDCA are calculated as follows:

 $HMF \text{ conversion} = \frac{(1 - \frac{Moles \text{ of } HMF}{Moles \text{ of } HMF \text{ loaded}}) \times 100\%}{\frac{Moles \text{ of } FDCA}{Moles \text{ of } FDCA}}$   $FDCA \text{ selectivity} = \frac{Moles \text{ of } HMF \text{ converted}}{Moles \text{ of } FDCA} \times 100\%$   $FDCA \text{ yield} = \frac{Moles \text{ of } HMF \text{ loaded}}{Moles \text{ of } HMF \text{ converted}} \times 100\%$   $Turnover \text{ frequency} = \frac{Moles \text{ of } HMF \text{ converted}}{Moles \text{ of } active \text{ sites}} \times \frac{1}{reaction \text{ time}}$ 



**Fig. S1** (a) Low-angle and (b) high-angle powder XRD patterns, (c) nitrogen adsorption/desorption isotherms and pore size distribution and (d) FT-IR spectra of Co-based materials.



**Fig. S2** (a) SEM and (b) TEM images of the ZIF-67@KIT-6 material, (c) simulated FFT patterns of the ZIF-67 crystal. The reciprocal distance between two (440) spots is 0.667 Å<sup>-1</sup>, revealing that the lattice distance of (440) planes for the ZIF-67 crystal is 2.99 Å.



Fig. S3 XPS patterns of the Co 2p region of Co@KIT-6.



Fig. S4 TEM images of (a) parent KIT-6 ultrathin cuts, (b) Co/KIT-6 and (c) HRTEM of an individual  $Co_3O_4$  nanoparticle.



**Fig. S5** The photographs of the as-prepared nanocomposites. From left to right: KIT-6, ZIF-67, ZIF-67@KIT-6, Co@KIT-6, MIL-88b@KIT-6, Fe@KIT-6, Ni-ZIF@KIT-6, Ni@KIT-6, HKUST-1@KIT-6, and Cu@KIT-6.



**Fig. S6** (a) XRD patterns of MIL-88b@KIT-6 and simulated MIL-88b, (b) FT-IR spectra of KIT-6, MIL-88b@KIT-6 and MIL-88b (from top to bottom. For the parent KIT-6, the two major absorption bands at 1080 and 790 cm<sup>-1</sup> revealed stretching vibrations of Si-O-Si bonds. For pure MIL-88b, the band at 550 cm<sup>-1</sup> was assigned to the vibration of Fe-O bonds. The strong bands at 1399 and 1663 cm<sup>-1</sup> were related to the vibration of C-O and C=O bonds), (c, d) Low- and high-angle XRD patterns of Fe@KIT-6, (e, f) TEM images of Fe@KIT-6 ultrathin cuts, in which homogeneously dispersed Fe<sub>3</sub>O<sub>4</sub> NPs could be obviously observed as dark spots, (g) HR-TEM image of an individual Fe<sub>3</sub>O<sub>4</sub> nanoparticle, (h) XPS patterns of Fe 2p region, (i-1) STEM image and elemental mappings of Fe, Si and O of Fe@KIT-6 ultrathin cuts.



**Fig. S7** XRD patterns of HKUST-1@KIT-6 and simulated HKUST-1, (b) FT-IR spectra of KIT-6, HKUST-1@KIT-6 and HKUST-1 (from top to bottom. For the parent KIT-6, the two major absorption bands at 1080 and 790 cm<sup>-1</sup> revealed stretching vibrations of Si-O-Si bonds. For pure HKUST-1, the band at 620 cm<sup>-1</sup> was assigned to the vibration of Cu-O bonds. The strong bands at 1449 and 1647 cm<sup>-1</sup> were related to the vibration of C=C and C=O bonds), (c, d) Low- and high-angle XRD patterns of Cu@KIT-6, (e, f) TEM images of Cu@KIT-6 ultrathin cuts, in which homogeneously dispersed CuO naoparticles could be obviously observed as dark spots, (g) HR-TEM image of an individual CuO nanoparticle, (h) XPS patterns of Cu@KIT-6 ultrathin cuts.



**Fig. S8** XRD patterns of Ni-ZIF@KIT-6 and Ni-ZIF, (b) FT-IR spectra of KIT-6, Ni-ZIF@KIT-6 and Ni-ZIF (from top to bottom. For the parent KIT-6, the two major absorption bands at 1080 and 790 cm<sup>-1</sup> revealed stretching vibrations of Si-O-Si bonds. For pure Ni-ZIF, the band at 598 cm<sup>-1</sup> was assigned to the vibration of Ni-N bonds. The weak band at 1590 was related to the vibration of C=N bond), (c, d) Low- and high-angle XRD patterns of Ni@KIT-6, (e, f) TEM images of Ni@KIT-6 ultrathin cuts, in which homogeneously dispersed NiO naoparticles could be obviously observed as dark spots, (g) HR-TEM image of an individual NiO nanoparticle, (h) XPS patterns of Ni 2p region, (i-1) STEM image and elemental mappings of Ni, Si and O of Ni@KIT-6 ultrathin cuts.



**Fig. S9** TEM images of (a, b) Co@KIT-6-275, (c, d) Co@KIT-6-300, (e, f) Co@KIT-6-2 and (g, h) Co@KIT-6-3.



**Fig. S10** (a) Hysteresis loops of Co@KIT-6 and Co/KIT-6, and (b) TG-DSC curves of the recycled Co@KIT-6 (red) and Co/KIT-6 (blue) catalysts.



**Fig. S11** TEM image (a), STEM image (b), and elemental mappings of Co (c) and Si (d) on ultrathin cuts of the Co@KIT-6 catalyst after six runs.



Fig. S12 TEM image of the Co/KIT-6 catalyst after six runs.

Sample	$S_{BET}$ $(m^2 g^{-1})$	$S_{Langmuir}$ $(m^2 g^{-1})$	V <sub>pore</sub> (cm <sup>3</sup> g <sup>-1</sup> )	D <sub>pore</sub> (nm)
ZIF-67@KIT-6	301	425	0.40	6.1
Co@KIT-6	522	694	0.58	7.3
Co/KIT-6	550	734	0.66	7.0
KIT-6-blank	602	780	0.70	7.7
KIT-6	608	781	0.70	7.8
MIL-88b@KIT-6	326	449	0.42	6.3
Fe@KIT-6	531	701	0.56	7.1
HKUST-1@KIT-6	342	467	0.46	6.2
Cu@KIT-6	539	716	0.58	7.0
NiZIF@KIT-6	335	451	0.41	6.1
Ni@KIT-6	533	708	0.57	7.2

 Table S1. Surface areas and pore volumes of the obtained materials.

	Element content (%)						
Sample –	С	Со	Fe	Cu	Ni		
ZIF-67	43.4	26.7	-	-	-		
ZIF-67@KIT-6	16.5	10.1	-	-	-		
Co@KIT-6	-	13.6	-	-	-		
Co/KIT-6	-	13.6	-	-	-		
KIT-6-blank	-	-	-	-	-		
MIL-88b@KIT-6	3.4	-	10.7	-	-		
Fe@KIT-6	-	-	11.3	-	-		
HKUST-1@KIT- 6	10.8	-	-	9.4	-		
Cu@KIT-6	-	-	-	11.6	-		
NiZIF@KIT-6	16.9	-	-	-	10.5		
Ni@KIT-6	-	-	-	-	13.4		

**Table S2.** Elemental compositions of the as-synthesized materials measured by AAS

 and elemental analysis.

Dof	Catalyst	T (°C), Time		Con.	Yield	TOF (h <sup>-</sup>
Kel.	Catalyst	atmosphere	(h)	(%)	(%)	1)
	Co@KIT-6	80, 0.1 MPa air	2	100	>99	150
This	Fe@KIT-6	95, 0.1 MPa air	2	90	89	135
work	Cu@KIT-6	110, 0.1 MPa air	2	87	82	131
	Ni@KIT-6	100, 0.1 MPa air	2	85	80	128
53	AuPd/ZOC	80, 0.3 MPa O <sub>2</sub>	4	>99	>99	49.8
50	Au/CeO <sub>2</sub>	65, 1 MPa air	48	100	>99	18.75
58	Au/TiO <sub>2</sub>	65, 1 MPa air	8	100	>99	18.75
59	Au/HY	60, 0.3 MPa O <sub>2</sub>	6	>99	>99	18.3
55	Pt/CNTs	95, 0.5 MPa O <sub>2</sub>	14	100	98	7.14
61	γFe <sub>2</sub> O <sub>3</sub> @HAP	100, O <sub>2</sub> flow	6	07	02.0	6.54
	-Pd	(30 mL·min <sup>-1</sup> )	0	97	92.9	
60	Au/HT	65, O <sub>2</sub> flow	7	>99	>99	5.70
		(50 mL·min <sup>-1</sup> )	/			
54	Pt@PMO-IL-	80, 0.1 MPa O <sub>2</sub>	24	>99	>99	4.17
	2					
56	Pt/C-O-Mg	110, 1.0 MPa O <sub>2</sub>	6	100	97	4.04
57	Ru/C	120, 0.2 MPa O <sub>2</sub>	5	100	88	1.00

**Table S3.** Comparison of results in HMF oxidation to FDCA over different catalysts.<sup>a</sup>

 ${}^{a}\text{TOF} = n_{\text{HMF converted}}/(n_{\text{active sites}} \cdot time)$ 

Entry	Temperatur e (°C)	Solvent	Time (h)	HMF conversion (%)	FDCA selectivity (%)	FDCA yield (%)
1	60	H <sub>2</sub> O	2	63	>99	62
2	70	$H_2O$	2	85	>99	84
3	80	$H_2O$	1	52	>99	51
4	80	H <sub>2</sub> O	1.5	76	>99	75
5	80	$H_2O$	2	100	>99	>99
6	80	Toluene	2	75	92	69
7	80	Ethanol	2	83	90	75
8	80	Cyclohexane	2	52	83	43

 Table S4. HMF oxidation over Co@KIT-6.

Reaction conditions: HMF (1.0 mmol), catalyst (metal, 1 mol%), air (0.1 MPa), solvent (3 mL).

Sample	Co content before reaction (wt%)	Co content after reaction (wt%)	Amount of Co leached (wt%)	Leaching percentage (%)
Co@KIT-6	13.6	13.5	0.1	<1
Co/KIT-6	13.6	12.5	1.1	8.1

 Table S5. The Co contents before and after the reaction.