Supporting Information

Highly Selective Synthesis of 2,5-Bis(aminomethyl)-furan via Catalytic Amination of 5-Hydroxymethyl-furfural with NH_3 over A Bifunctional Catalysts

Hangkong Yuan,[a] Bright T. Kusema,*[b] Zhen Yan,[b] Stéphane Streiff,[b] and Feng Shi*[a]

[a]State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, No.18, Tianshui Middle Road, Lanzhou, 730000, China;
[b]Eco-Efficient Products and Processes Laboratory (E2P2L), UMI 3464 CNRS-Solvay, 3966 Jin Du Road, Xin Zhuang Ind. Zone, 201108 Shanghai, China

Contents

1. General information and experimental section

General Information:

TEM was carried out by using a Tecnai G2 F30 S-Twin transmission electron microscope operating at 300 kV. For TEM investigations, the catalysts were dispersed in ethanol by ultrasonication and deposited on carbon-coated copper grids. XRD measurements were conducted by using a STADIP automated transmission diffractometer (STOE) equipped with an incident beam curved germanium monochromator with CuK_{a1} radiation and current of 40 kV and 150 mA, respectively. The XRD patterns were scanned in the 2 Theta range of 10-90 °. XPS were obtained using a VG ES-CALAB 210 instrument equipped with a dual Mg/Al anode X-ray source, a hemispherical capacitor analyzer, and a 5 keV Ar^+ iron gun. The electron binding energy was referenced to the C1s peak at 284.8 eV. The background pressure in the chamber was less than 10^{-7} Pa. The BET surface area measurements were performed on a Quantachrome IQ_2 at the temperature of 77 K. The pore size distribution was calculated from the adsorption-desorption isotherm by using the Barrett, Joyner, and Halenda (BJH) method. Prior to measurements, the samples were degassed at 180 °C for 2 h， then 300 °C for 3 h, at a rate of 10 $^{o}C•min^{-1}$. The bulk metal composition of the catalysts was quantified by inductively coupled plasma analysis (ICP) using an Activa (Horiba Jobin-Yvon) Optical Emission Spectrometer. Before the measurements, the samples were dissolved using a mixture of inorganic acids (H_2SO_4, HNO_3 and HF).

Experimental Section:

$Ni(NO_3)_2·6H_2O$, $Cu(NO_3)_2·3H_2O$, $Al(NO_3)_3·9H_2O$, NaOH and Na_2CO_3, all supplied by Sinopharm Chemical Reagent Co., Ltd. were used for the preparation of the catalysts. 5-hydroxymethylfurfural, 2,5-furandimethanamine, and 5-aminomethyl-2-furylmethanol were procured from Shanghai Shaoyuan Co., Ltd. Dioxane was purchased from Ark Pharm, Inc., ethanol was purchased from Damao Chemical Reagent Factory, hydrogen and NH_3 were obtained commercially from LanZhou YuLong Gas Co., Ltd. All solvents and chemicals were obtained commercially and were used as received.

Typical procedure for catalyst preparation

Synthesis of $Cu_4Ni_1Al_4O_x$ sample:

A typical $Cu_4Ni_1Al_4O_x$ mixed oxide catalyst was synthesized by a co-precipitation method. In detail, a 200 mL mixed aqueous solution of copper, nickel and aluminum nitrates (with the Cu^{2+}+Ni^{2+}+Al^{3+} concentration fixed at 0.36 M, the Cu/Ni/Al molar ratio as 4/1/4) was placed into a 500 mL flask, and the 180 mL base solution (Na^+ = 1.5 M, with the NaOH/Na_2CO_3 mole ratio = 5.59/1) was added dropwise into the salt solution at RT under vigorous stirring within 1 hour, and the resultant slurry with stirring maintain overnight. Then the solid precipitate was washed thoroughly with deionized water until the pH value of the filtrate was approximately 7. The filter cake was dried at 100 °C in air for 12 h and then underwent a reduction at 450 °C for 3 h (pure hydrogen at 10 mL/min, 10 °C/min). Before exposure to air, the sample must be cooled to RT completely.

Typical procedure for catalytic amination of HMF

Activity tests were performed in a 150 mL magnetic stirred autoclave equipped with a PID temperature controller. In a typical experiment, 10 g of HMF dissolved in 50 mL of dioxane, 915 mg sodium carbonate and 2 g catalyst was loaded before sealing the reactor. The autoclave was purged with H_2 three times to drive out the air then followed by NH_3 charging (23 g) and H_2 charging to an appropriate pressure at RT. Finally, the reactor was heated to the first stage of reaction temperature for 6 hours, and then raising the reaction temperature for the second reaction, the reaction was carried out at a stirring speed of 600 rpm. Subsequently, the reaction mixture was analyzed by GC-MS (Agilent 7890B/5977A) and GC-FID (Agilent 7890A). Recycling experiments of the solid catalyst were carried out in a similar manner but after removing the liquid solution by filtration. The solid catalyst was simply washed with ethanol, hot water, and 1,4-dioxane, and then introduced into the autoclave together with fresh HMF for a subsequent catalytic cycle. The conversion of HMF and selectivity and yield of the products were defined on carbon basis calculations, as shown in the formulas listed below.

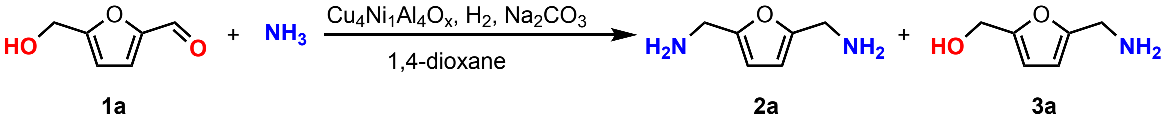
Conversion (%) = moles of HMF consumed /moles of HMF initially consumed

Selectivity (%) = moles of carbon in specific product /moles of carbon in consumed HMF

Yield (%) = [Conversion (%) × Selectivity (%)]/100.

2. Optimization of the reaction conditions

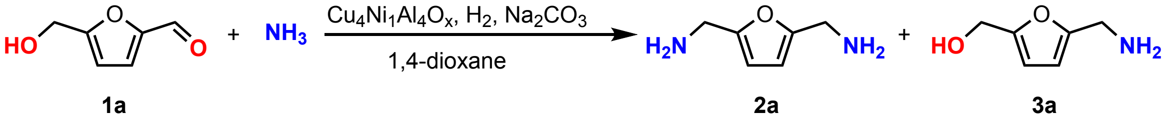
Table S1 Reaction condition optimization for direct amination of 5-HMF with NH_3 [a]



Entry	Catalyst loading (g)	Conv. [%][b]	Yield [%][b]		Mass balance [%]
			2a	**3a**	
1	1.5	100	65.9	10.4	76.3
2	2.0	100	75.2	8.1	83.3
3	2.5	100	78.8	5.7	84.5

[a] Reaction conditions: 5-HMF (10 g, 79.4 mmol), NH_3 (23 g, 1352.9 mmol), Na_2CO_3 (0.915 g, 8.6 mmol, 11 mol% to 5-HMF), H_2 (4.5 MPa), 1,4-dioxane (50 mL), 90 °C, 6 h then 210 °C, 18 h. [b] Determined by GC-FID using biphenyl as the internal standard material.

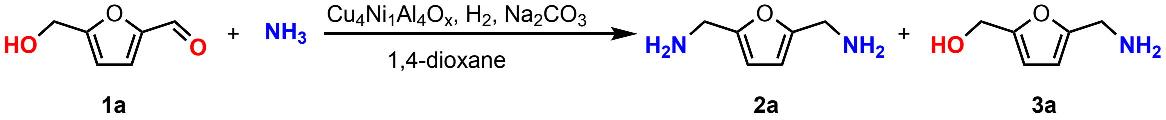
Table S2 Reaction condition optimization for directamination of 5-HMF with NH_3 [a]



Entry	Na_2CO_3 loading (mg)	Conv. [%][b]	Yield [%][b]		Mass balance [%]
			2a	**3a**	
1	500	100	50.0	5.5	55.5
2	700	100	62.5	5.5	68.0
3	915	100	75.2	8.1	83.3
4	1100	100	71.4	5.7	77.1

[a] Reaction conditions: 5-HMF (10 g, 79.4 mmol), NH_3 (23 g, 1352.9 mmol), $Cu_4Ni_1Al_4O_x$ (2.0 g, 20 wt% to 5-HMF), H_2 (4.5 MPa), 1,4-dioxane (50 mL), 90 °C, 6 h then 210 °C, 18 h. [b] Determined by GC-FID using biphenyl as the internal standard material.

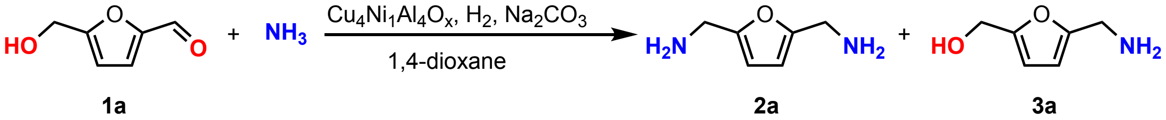
Table S3 Reaction condition optimization for directamination of 5-HMF with NH_3 [a]



Entry	NH_3 loading (g)	Conv. [%][b]	Yield [%][b]		Mass balance [%]
			2a	**3a**	
1	12	100	41.7	0.1	41.8
2	17	100	51.3	5.6	56.9
3	23	100	75.2	8.1	83.3
4	27	100	66.5	5.4	71.9

[a] Reaction conditions: 5-HMF (10 g, 79.4 mmol), $Cu_4Ni_1Al_4O_x$ (2.0 g, 20 wt% to 5-HMF), Na_2CO_3 (0.915 g, 8.6 mmol, 11 mol% to 5-HMF), H_2 (4.5 MPa), 1,4-dioxane (50 mL), 90 °C, 6 h then 210 °C, 18 h. [b] Determined by GC-FID using biphenyl as the internal standard material.

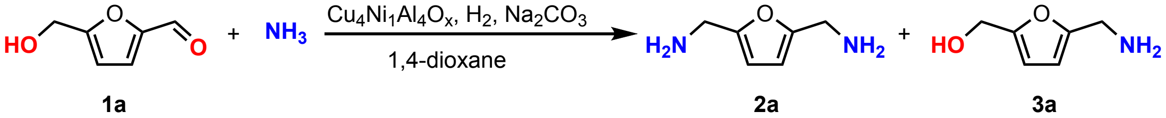
Table S4 Reaction condition optimization for directamination of 5-HMF with NH_3 [a]



Entry	H_2 (MPa)	Conv. [%][b]	Yield [%][b]		Mass balance [%]
			2a	**3a**	
1	3.0	100	24.3	40.7	65.0
2	4.5	100	75.2	8.1	83.3
3	5.5	100	72.9	5.5	78.4

[a] Reaction conditions: 5-HMF (10 g, 79.4 mmol), NH_3 (23 g, 1352.9 mmol), $Cu_4Ni_1Al_4O_x$ (2.0 g, 20 wt% to 5-HMF), Na_2CO_3 (0.915 g, 8.6 mmol, 11 mol% to 5-HMF), 1,4-dioxane (50 mL), 90 °C, 6 h then 210 °C, 18 h. [b] Determined by GC-FID using biphenyl as the internal standard material.

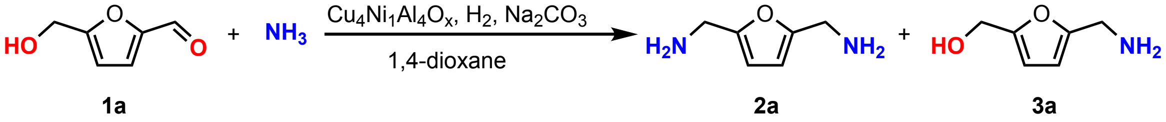
Table S5 Reaction condition optimization for directamination of 5-HMF with NH_3 [a]



Entry	T (°C)	Conv. [%][b]	Yield [%][b]		Mass balance [%]
			2a	**3a**	
1	170	100	15.6	82.3	97.9
2	190	100	35.9	62.9	98.8
3	210	100	75.2	8.1	83.3
4	220	100	66.5	5.7	72.2

[a] Reaction conditions: 5-HMF (10 g, 79.4 mmol), NH_3 (23 g, 1352.9 mmol), $Cu_4Ni_1Al_4O_x$ (2.0 g, 20 wt% to 5-HMF), Na_2CO_3 (0.915 g, 8.6 mmol, 11 mol% to 5-HMF), 1,4-dioxane (50 mL), 90 °C, 6 h then different temperature for 18 h. [b] Determined by GC-FID using biphenyl as the internal standard material.

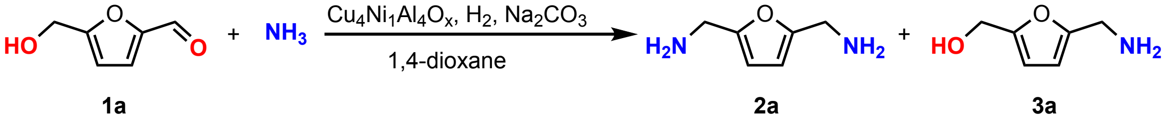
Table S6 Reaction condition optimization for directamination of 5-HMF with NH_3 [a]



Entry	Reaction time of second stage (h)	Conv. [%][b]	Yield [%][b]		Mass balance [%]
			2a	**3a**	
1	0	100	<0.1	>99.9	>99.9
2	6	100	57.8	24.2	82.0
3	12	100	67.9	14.1	82.0
4	18	100	75.2	8.1	83.3
5	24	100	73.2	0.1	73.3
6	34	100	74.9	0.1	75.0

[a] Reaction conditions: 5-HMF (10 g, 79.4 mmol), NH_3 (23 g, 1352.9 mmol), $Cu_4Ni_1Al_4O_x$ (2.0 g, 20 wt% to 5-HMF), Na_2CO_3 (0.915 g, 8.6 mmol, 11 mol% to 5-HMF), 1,4-dioxane (50 mL), 90 °C , 6 h then 210 °C for several hours. [b] Determined by GC-FID using biphenyl as the internal standard material.

Table S7 Reaction condition optimization for directamination of 5-HMF with NH_3 [a]



Entry	Reaction time of first stage (h)	Conv. [%][b]	Yield [%][b]		Mass balance [%]
			2a	**3a**	
1	0	100	8.5	6.6	15.1
2	3	100	70.4	5.6	76.0
3	6	100	75.2	8.1	83.3
4	9	100	85.9	9.5	95.4
5	12	100	67.1	5.5	72.6

[a] Reaction conditions: 5-HMF (10 g, 79.4 mmol), NH_3 (23 g, 1352.9 mmol), $Cu_4Ni_1Al_4O_x$ (2.0 g, 20 wt% to 5-HMF), Na_2CO_3 (0.915 g, 8.6 mmol, 11 mol% to 5-HMF), 1,4-dioxane (50 mL), 90 °C for several hours then 210 °C, 18 h. [b] Determined by GC-FID using biphenyl as the internal standard material.

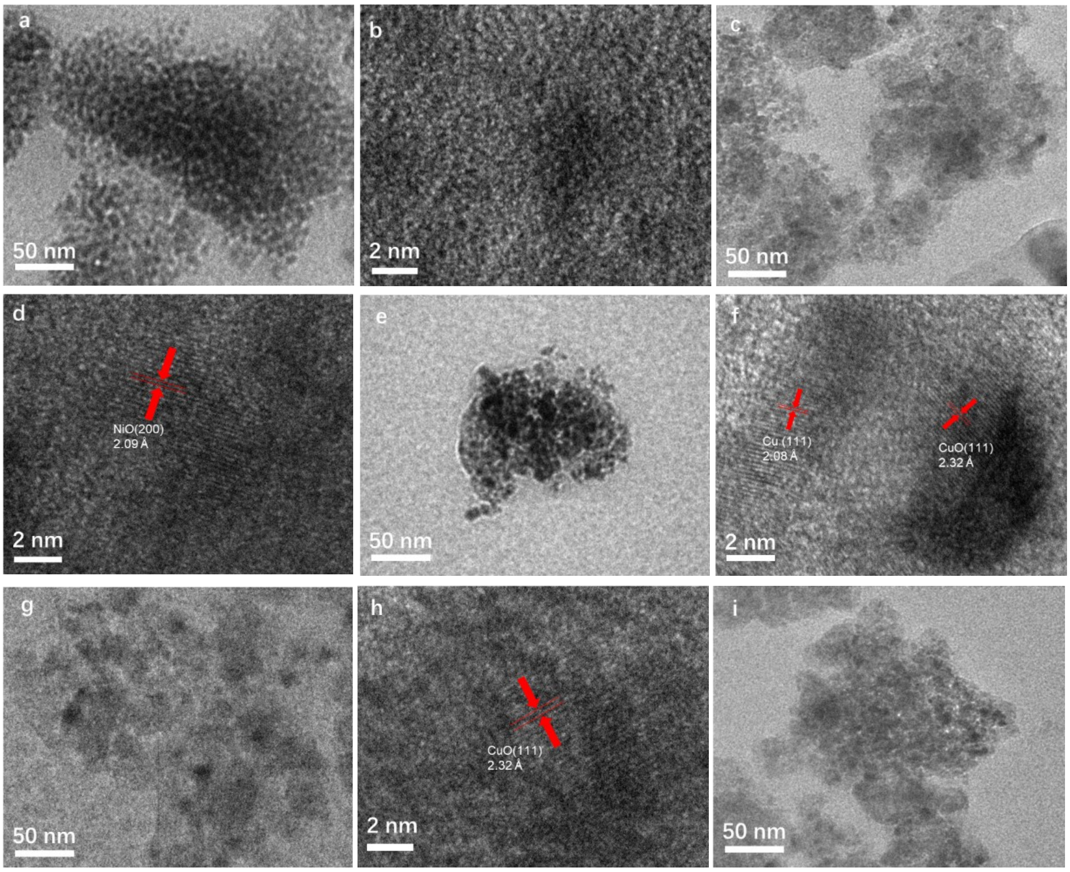
3. Characterization results of catalysts

Table S8 The physical properties of catalysts

Entry	Catalyst	Cu(wt%)[a]	Ni (wt%)[a]	SA (m^2 g^{-1}) [b]	APR (nm) [b]	PV (cm^3 g^{-1}) [b]
1	$Cu_1Ni_4Al_4O_x$	10.96	46.00	202.39	2.23	0.25
3	$Cu_1Ni_1Al_{1.6}O_x$	22.3	23.5	169.75	2.81	0.24
2	$Cu_4Ni_1Al_4O_x$	60.62	17.41	101.16	6.06	0.31
4	$Cu_6Ni_1Al_{5.6}O_x$	52.91	9.78	83.35	3.78	0.16
5	$Cu_{19}Ni_1Al_{16}O_x$	33.09	1.84	68.16	6.51	0.22
8	$Cu_1Al_1O_x$	35.89	-	79.77	9.29	0.37
9	$Ni_1Al_4O_x$	-	23.13	326.21	2.43	0.40
10	$Cu_4Ni_1Al_4O_x$ used three times	43.63	13.06	126.58	3.99	0.25

[a] Determined by ICP-AES. [b] Determined by an IQ_2 automated gas sorption analyser. SA: BET surface area; APS: average pore radius; PV: pore volume.

Fig. S1 TEM spectra of the catalysts. (a, b) $Cu_1Ni_4Al_4O_x$. (c, d) $Cu_1Ni_1Al_{1.6}O_x$. (e, f) $Cu_4Ni_1Al_4O_x$. (g, h) $Cu_6Ni_1Al_{5.6}O_x$. (i, j) $Cu_{19}Ni_1Al_{16}O_x$. (k,l) $Cu_1Al_1O_x$. (m,n) $Ni_1Al_4O_x$. (o, p) Used 3 time $Cu_4Ni_1Al_4O_x$.



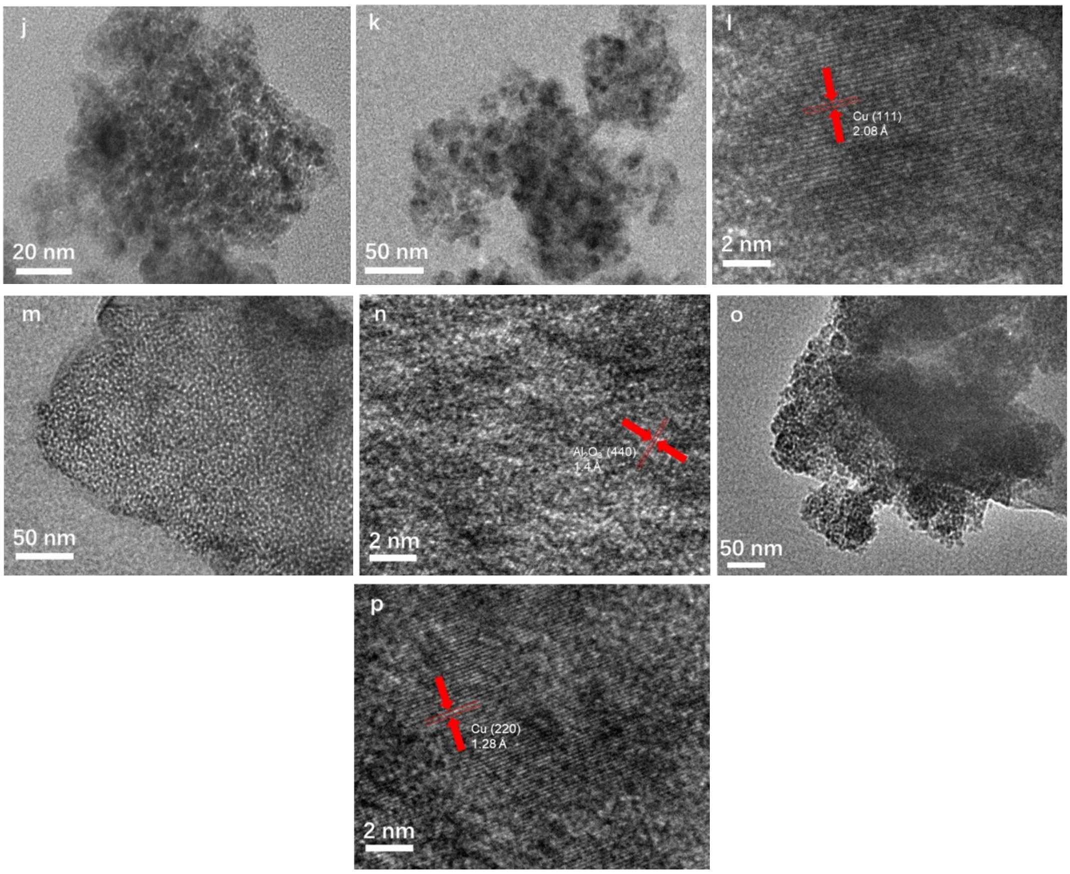


Fig. S2 XPS spectra of the catalysts. (a) $Cu_1Ni_4Al_4O_x$. (b) $Cu_1Ni_1Al_{1.6}O_x$. (c) $Cu_4Ni_1Al_4O_x$. (d) $Cu_6Ni_1Al_{5.6}O_x$. (e) $Cu_{19}Ni_1Al_{32}$. (f) Used 3 time $Cu_4Ni_1Al_4O_x$.

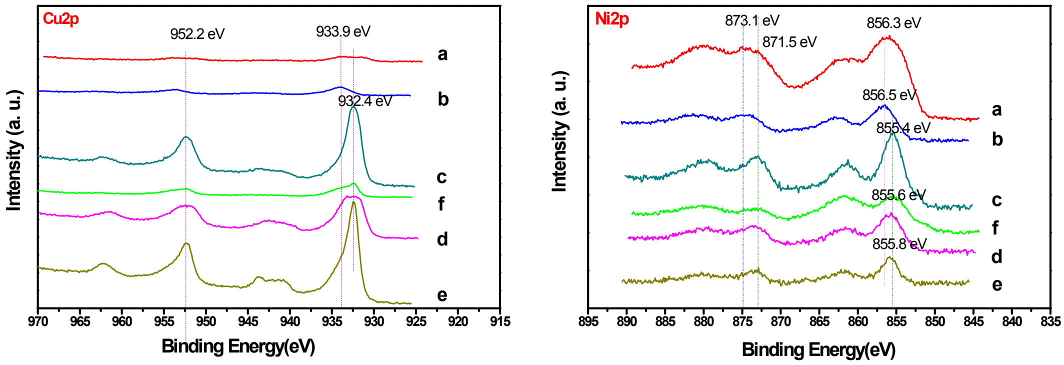
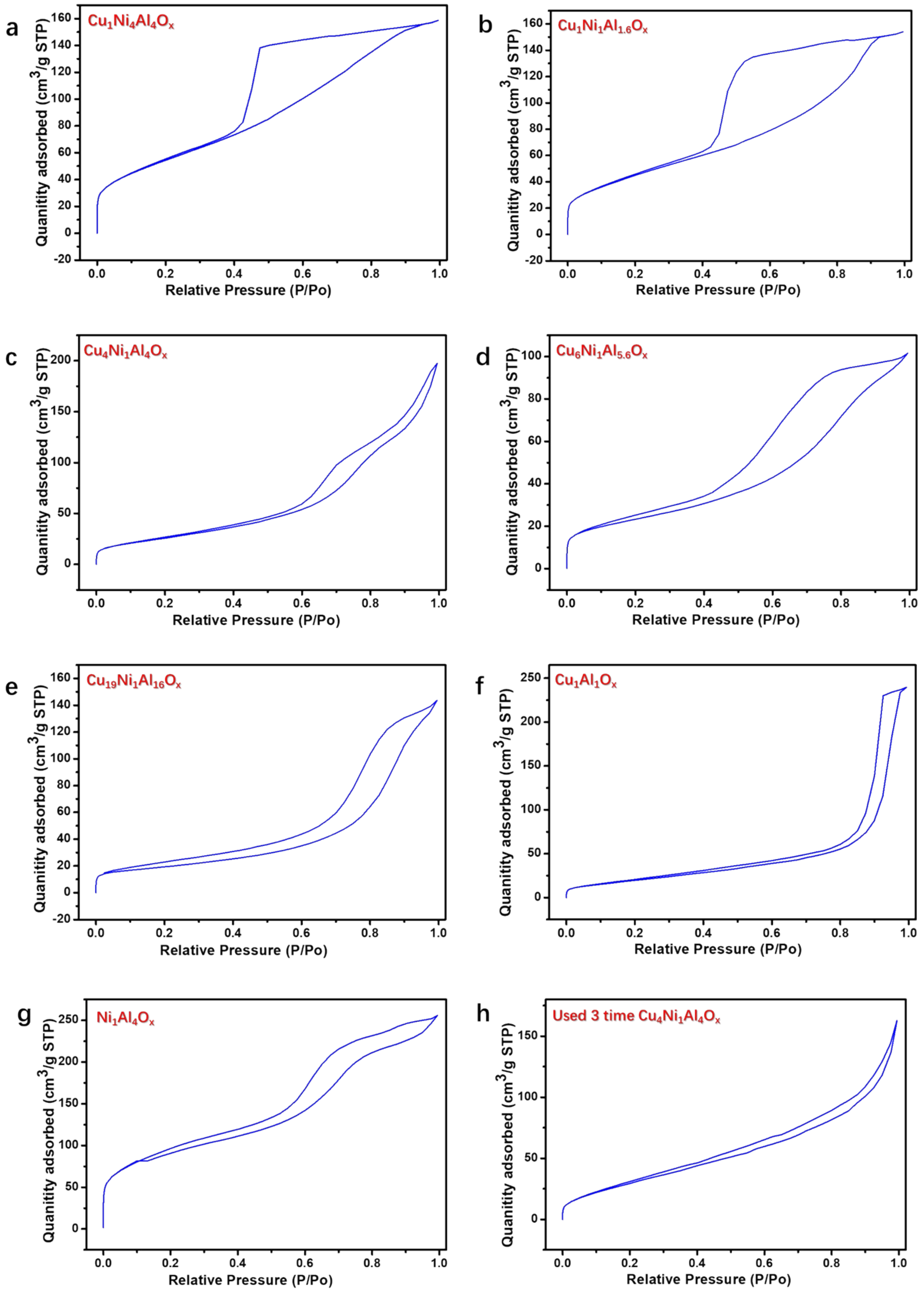


Fig. S3 The N_2 adsorption isotherm of the catalysts. (a) $Cu_1Ni_4Al_4O_x$. (b) $Cu_1Ni_1Al_{1.6}O_x$. (c) $Cu_4Ni_1Al_4O_x$. (d) $Cu_6Ni_1Al_{5.6}O_x$. (e) $Cu_{19}Ni_1Al_{16}O_x$. (f) $Cu_1Al_1O_x$. (g) $Ni_1Al_4O_x$. (h) Used 3 time $Cu_4Ni_1Al_4O_x$.



4. The leaching test

Fig. S4 The leaching test: After 2 h of reaction of HMF with NH_3 over $Cu_4Ni_1Al_4O_x$ at 210 ^oC and separating the solid catalysts, further reaction was operated on the residual liquids for another 16 h. Clearly, the reaction stopped after removing the solid catalyst. This observation demonstrates that the leached Cu and Ni should not be the active species.