Supporting Information

Silicalite-1 Encapsulated Cu Nanoclusters with La Modification for Enhanced Performance in Hydrogenation of Furfural to Furfuryl Alcohol

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Experimental

Catalysts preparation

Preparation of Cu@S-1

The silicate-loaded Cu-based zeolite catalysts were synthesized through an in-situ encapsulation method. Ethyl orthosilicate (TEOS, 99%, Maclin) and tetrapropylammonium hydroxide (TPAOH, 40% aq, Kente) were selected as the Si source and templating agent, respectively. First, 11.25 g of TPAOH was added to 7.5 g of H_2O and strongly stirred to obtain a clear solution. Then, a synthetic gel ($5.5TPAOH:5.0SiO_2:41.7H_2O$) was prepared by adding 10.4 g of TEOS to the solution and stirring at 25 °C for 4 h. Next, 0.22 g of $Cu(NO_3)_2 \cdot 3H_2O$ (99%, SCR) was added to 2 g of H_2O to obtain a $Cu(NO_3)_2$ solution and mixed with 0.7 g of ethylenediamine (EDA, 99%, SCR) and the synthesized gel. After stirring for 3 h, the mixture was put into an autoclave, heated in a constant temperature blast drying oven to 100 °C, and kept at this temperature for 48 h. The mixed solution was centrifuged to isolate the solid catalyst and then dried to remove the residual water. Finally, the powder was calcinated in air at 500 °C for 6 h, and then pretreated by reduction in a 10% H_2/Ar atmosphere (Flow rate: 50 $mL \cdot min^{-1}$) at 450 °C for 5 h (Heating rate: 1 $°C \cdot min^{-1}$). The resulting catalyst was named Cu@S-1.

Preparation of La-Cu@S-1

The calcined Cu@S-1 catalyst was mixed with 0.05 mol/L $La(NO_3)_3$ (99%, Maclin) solution at a solid-liquid mass ratio of 1:50. The impregnation operation was carried out at room temperature for 6 h. After that, the mixed solution was centrifuged to isolate the solid catalyst and then dried to remove the residual water. Finally, the powder was pretreated by reduction in a 10% H_2/Ar atmosphere (Flow rate: 50 mL/min) at 450 °C for 5 h (Heating rate: 1 °C/min). The resulting catalyst was named La-Cu@S-1.

Preparation of Cu@ZSM-5

The ZSM-5-loaded Cu-based zeolite catalysts were synthesized through an in-situ encapsulation method. TEOS, sodium aluminate ($NaAlO_2$, Al (Al_2O_3): 50-56%, Na (Na_2O): 37-45%, Sigma-Aldrich), and TPAOH were selected as the Si source, Al source, and templating agent, respectively. First, 0.11 g of $NaAlO_2$ and 11.25 g of TPAOH were added to 7.5 g of H_2O and strongly stirred to obtain a clear solution. Then, a synthetic gel ($5.5TPAOH:5.0SiO_2:0.1Al:41.7H_2O$) was prepared by adding

10.4 g of TEOS to the solution and stirring at 25 °C for 4 h. Next, 0.22 g of $Cu(NO_3)_2 \cdot 3H_2O$ was added to 2 g of H_2O to obtain a $Cu(NO_3)_2$ solution and mixed with 0.7 g of EDA and the synthesized gel. After stirring for 3 h, the mixture was put into an autoclave, heated in a constant temperature blast drying oven to 100 °C, and kept at this temperature for 48 h. The mixed solution was centrifuged to isolate the solid catalyst and then dried to remove the residual water. Finally, the powder was calcinated in air at 500 °C for 6 h, and then pretreated by reduction in a 10% H_2/Ar atmosphere (Flow rate: 50 mL/min) at 450 °C for 5 h (Heating rate: 1 °C/min). The resulting catalyst was named Cu@ZSM-5.

Preparation of La-Cu@ZSM-5

The calcined Cu@ZSM-5 catalyst was mixed with 0.05 mol/L $La(NO_3)_3$ solution at a solid-liquid mass ratio of 1:50. The impregnation operation was carried out at room temperature for 6 h. After that, the mixed solution was centrifuged to isolate the solid catalyst and then dried to remove the residual water. Finally, the powder was pretreated by reduction in a 10% H_2/Ar atmosphere (Flow rate: 50 mL/min) at 450 °C for 5 h (Heating rate: 1 °C/min). The resulting catalyst was denoted as La-Cu@ZSM-5.

Catalyst testing

The liquid-phase hydrogenation of FFL was performed in a 50 mL PTFE-lined high-pressure reactor. First, 0.3 g of catalyst was mechanically mixed with 0.3 g of FFL (99%, Aladdin), using 23.56 g of isopropanol (99%, Aladdin) as the solvent. Next, N_2 and H_2 were purged three times continuously in sequence to remove the air and the residual N_2, respectively. The kettle was then pressurized with H_2 to an in-kettle pressure of 20 bar and heated to 110 °C. The reaction was carried out at 110 °C for 3 h with a stirring speed of 1000 rpm. After cooling down to room temperature, the kettle gas was discharged, and the mixture was centrifuged to separate the liquid supernatant from the catalyst. The reusability of Na-Cu@S-1 catalyst was investigated under the aforementioned reaction conditions; the catalysts after each reaction were separated by centrifugation, washing with isopropanol, and dried at room temperature overnight. Qualitative analyses of the products were carried out by the corresponding gas chromatographic (GC) on SH-Rxi-5Sil MS with a HP-5 column (30 m×0.25 mm×0.25 μm) and a flame ionization detector (FID). The standard curve (**Fig. S1**) was prepared

using the internal standard method. Octanol (99%, Aladdin) was used as the internal standard. The details for calculating the HMF conversion, product selectivity, and yield, as well as the turnover frequency (TOF), are as follows:

$$\text{FFL conversion (\%)} = \frac{\text{Moles of converted FFL}}{\text{Moles of initial FFL}} \times 100\%$$

$$\text{Product selectivity (\%)} = \frac{\text{Moles of the desired product}}{\text{Moles of converted FFL}} \times 100\%$$

$$\text{Product yield (\%)} = \frac{\text{Moles of the desired product}}{\text{Moles of initial FFL}} \times 100\%$$

$$\text{TOF} = \frac{\text{Moles of converted FFL}}{\text{Moles of total Cu} \times \text{Cu dispersion} \times \text{Reaction time}} \times 100\%$$

Characterization techniques

Cu and La contents were determined by an inductively coupled plasma-optical emission spectroscopy (ICP-OES, Agilent 5110). The structural morphology of the catalyst samples was analyzed using an Empyrean type X-ray diffractometer (XRD). The test parameters were listed as follows: operating voltage of 40 kV, operating current of 100 mA, scanning angle of 5-50° (2θ), scanning angular speed of 5 °/min, and scanning step of 0.02°. A Cu target was equipped, and a ceramic-structured X-ray tube was used with a phototube power of 2.2 kW. The morphology of the catalysts was examined by scanning transmission electron microscopy (STEM) and the corresponding energy spectral analysis (EDS-mapping) on a JEOL JEM-ARM200F microscope with an accelerating voltage of 200 kV, a resolution of 0.06 nm, and a Cs detector corrector. The specific surface area and pore structure of the catalysts were analyzed using Micromeritics 3-Flex. The samples were pre-treated under vacuum at 350 °C for 8 h, followed by N_2 adsorption-desorption test with liquid nitrogen. The X-ray photoelectron spectroscopy (XPS) and X-ray induced Auger electron spectroscopy (XAES) spectra were collected on Thermo Fisher ESCALAB 250Xi with an aluminum anode (Al Ka = 1486.6 eV). An AUTOCHEM II2920 DISCOVERY instrument was employed to perform the Temperature-programmed reduction of hydrogen (H_2-TPR) experiments. Before TPR measurements, 100 mg samples were treated with Ar (30 mL/min) at 300 °C for 30 min and then cooled down to 50 ℃ under the protection of Ar (30 mL/min). After flowing a 10% H_2/Ar mixture (50 mL/min) to allow the baseline to stabilize, the samples were gradually heated to 700 °C at a ramp rate of 10 °C/min in the 10% H_2/Ar (30 mL/min) atmosphere, and the signal was detected by a thermal

conductivity detector (TCD). Fourier transform infrared (FT-IR) spectroscopy of CO chemisorption was recorded on a Bruker Tensor II IR spectrometer equipped with a DTGS detector. Before CO chemisorption, the wafer was placed inside a self-made cell with a CaF_2 window. The sample was first reduced at 300 °C under a 10% H_2/Ar mixture (30 mL/min) for 1 h, evacuated with a high-vacuum pump, and cooled down with liquid nitrogen and connected to a gas chamber that permitted adjustment of the pressure of CO injected into the cell. CO adsorption was studied at 87 K at stepwise increasing CO pressures with the sample in a transmission mode.

Computational details.

The charge density difference and Bader charge analysis of MFI and La-MFI systems were calculated using the Vienna Ab initio Simulation Package (VASP) [1]. The electron exchange-correlation interactions and ion-electron interactions were described by the Perdew–Burke–Ernzerhof (PBE) functional [2] and the projector augmented wave (PAW) method [3]. A plane-wave cutoff energy of 400 eV was used for all calculations. Van der Waals interactions were accounted for using the DFT-D3 method developed by Grimme [4].

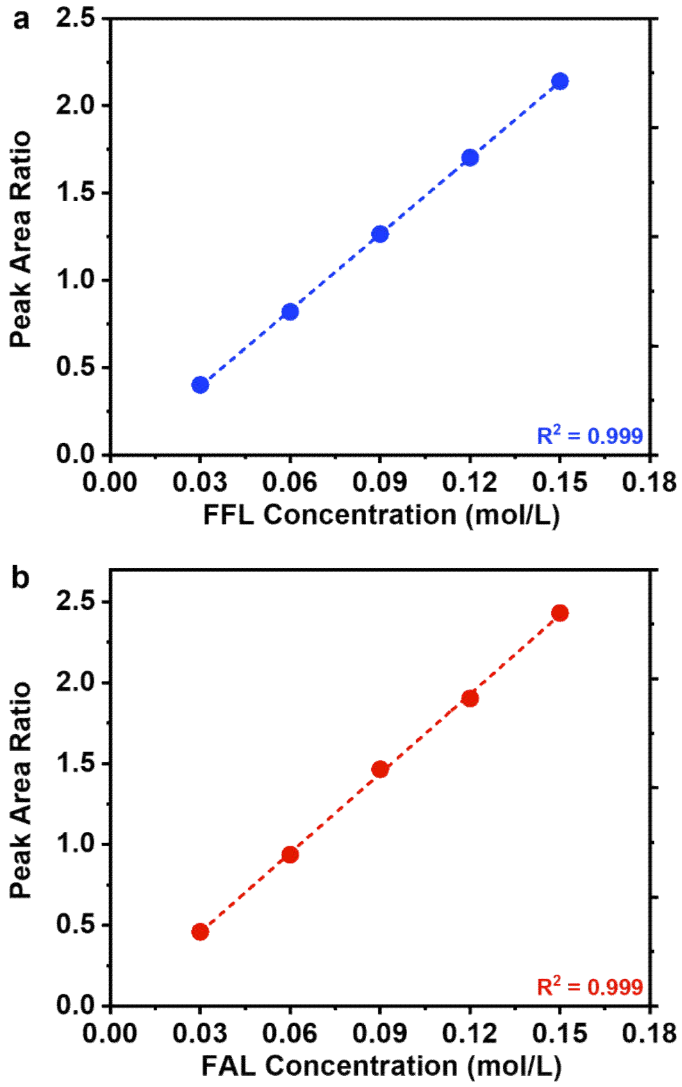

Fig. S1. Calibration curves of (a) FFL and (b) FAL by GC internal standard method..

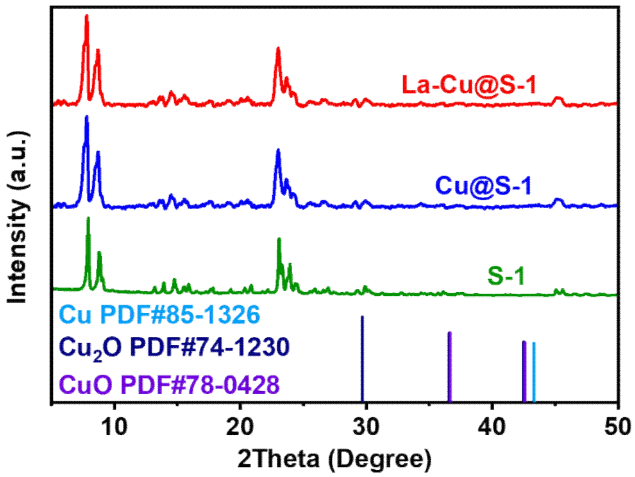

Fig. S2. XRD patterns of S-1, Cu@S-1, and La-Cu@S-1.

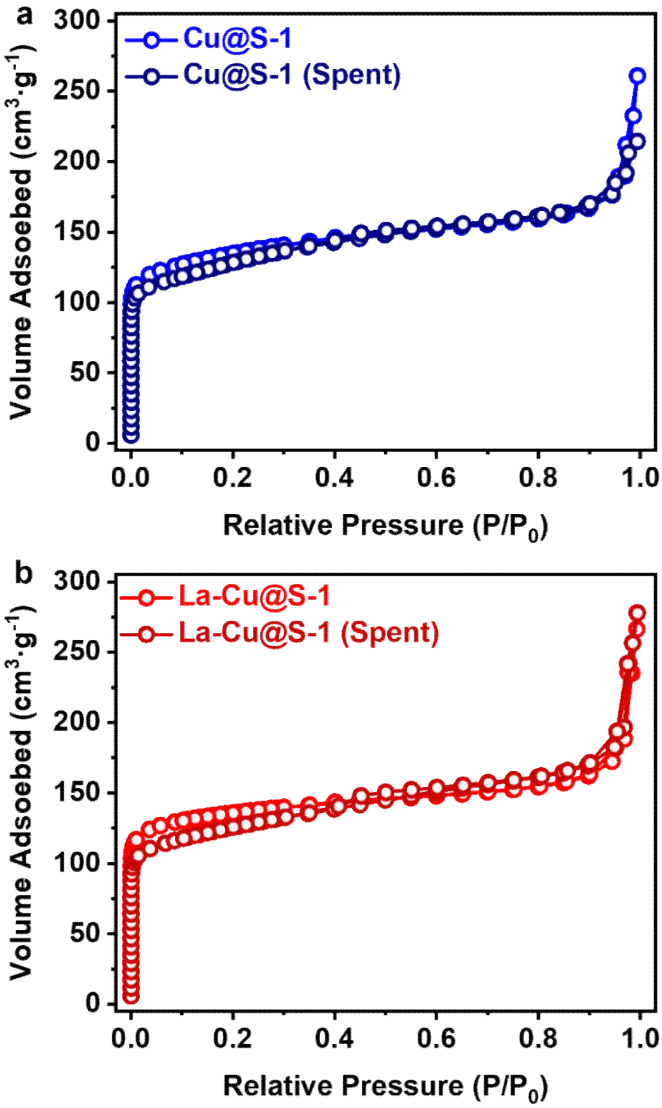

Fig. S3. N_2 adsorption and desorption curves of different Cu-zeolite catalysts.

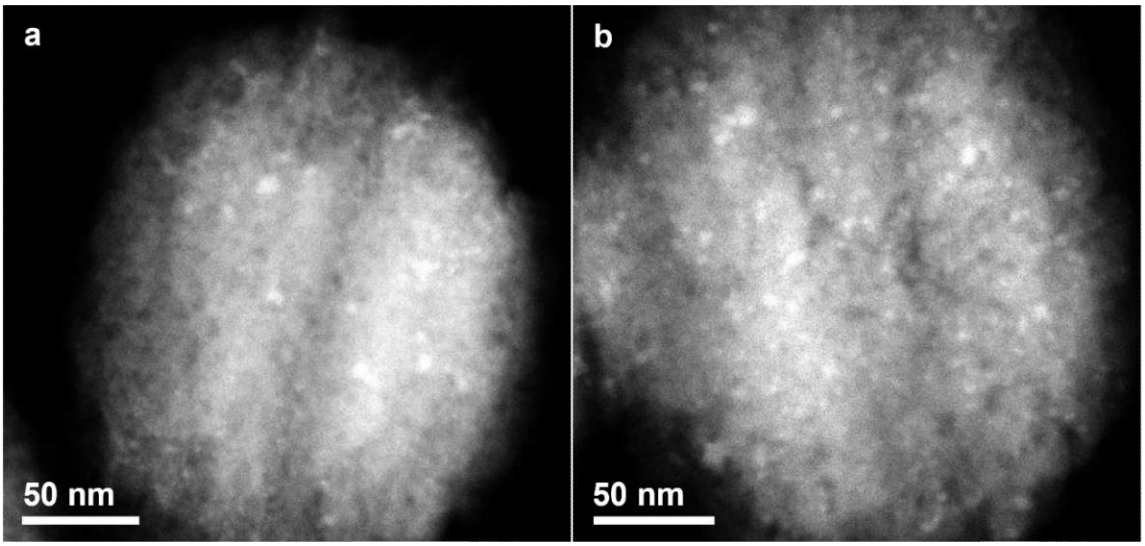

Fig. S4. HAADF-STEM images of Cu@S-1.

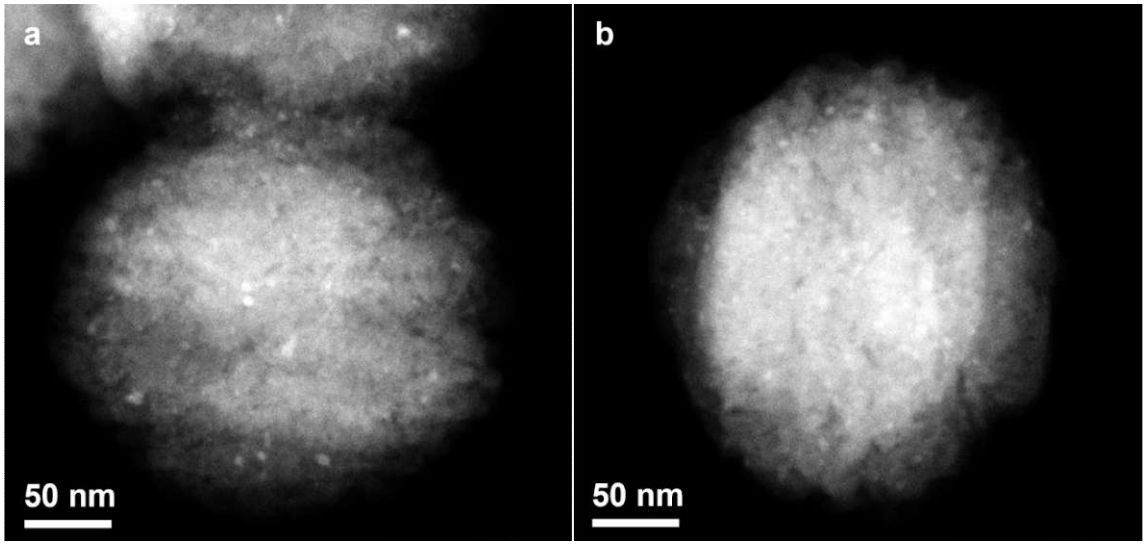

Fig. S5. HAADF-STEM images of La-Cu@S-1.

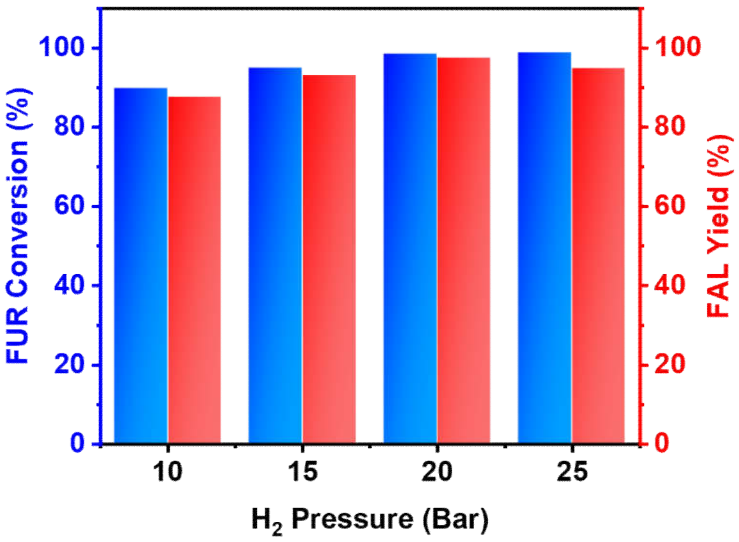

Fig. S6. Effect of H_2 pressure on catalytic performance of La-Cu@S-1. Reaction conditions: furfural mass = 0.3 g, isopropanol mass = 23.56 g, catalyst mass = 0.3 g, T = 110 ℃, P_{H2}= 10-25 bar, t = 3 h, Stirring speed = 1000.

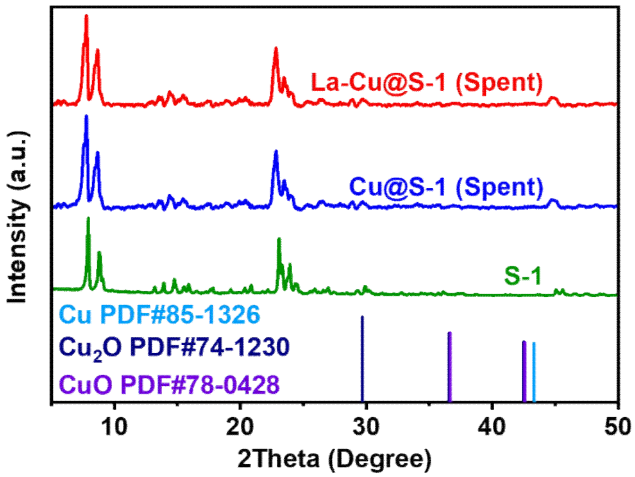

Fig. S7. XRD patterns of S-1, Cu@S-1 (Spent), and La-Cu@S-1 (Spent).

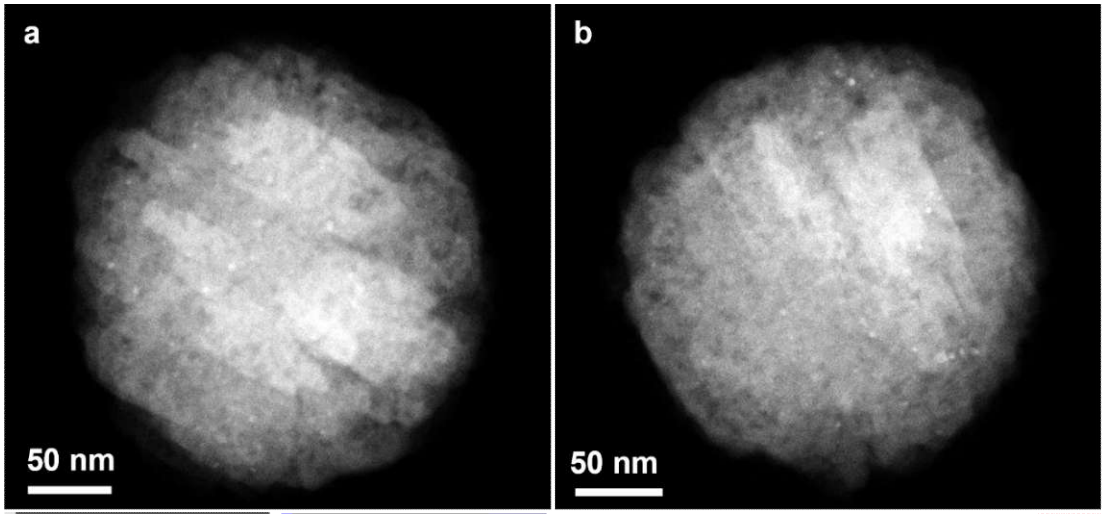

Fig. S8. HAADF-STEM images of Cu@S-1 (Spent).

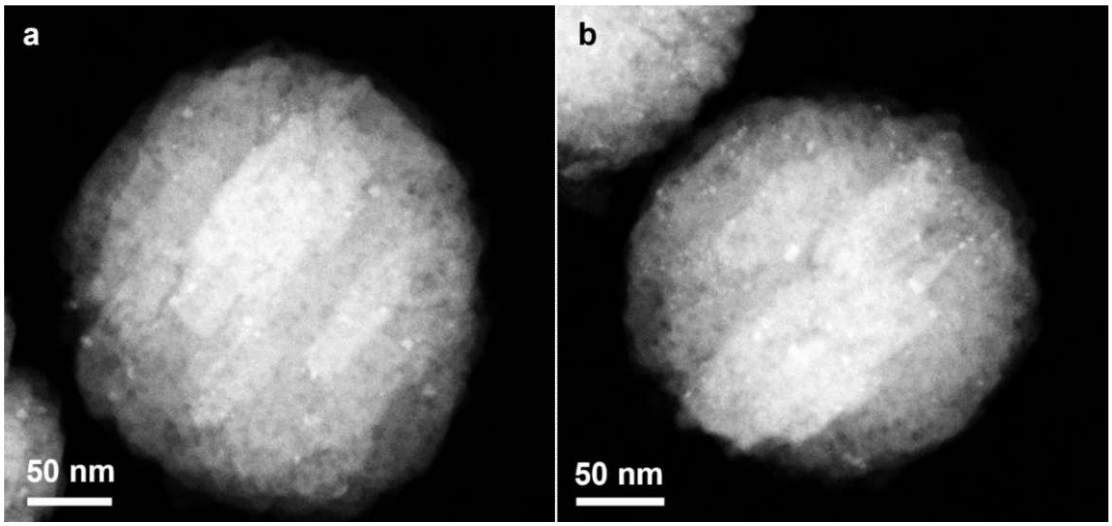

Fig. S9. HAADF-STEM images of La-Cu@S-1 (Spent).

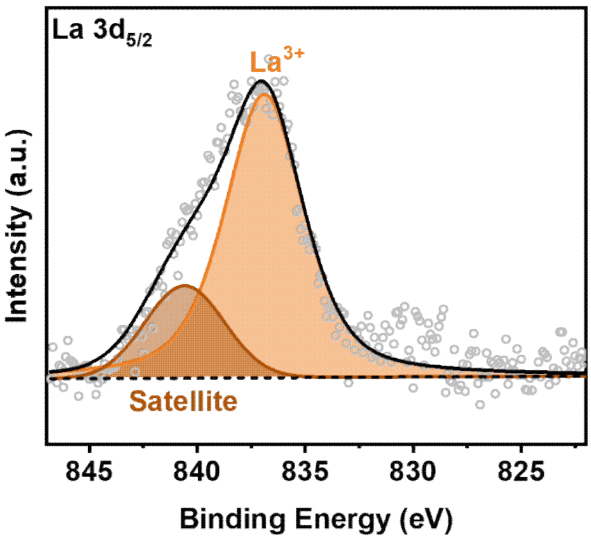

Fig. S10. La $3d_{5/2}$ XPS spectrum of La-Cu@S-1.

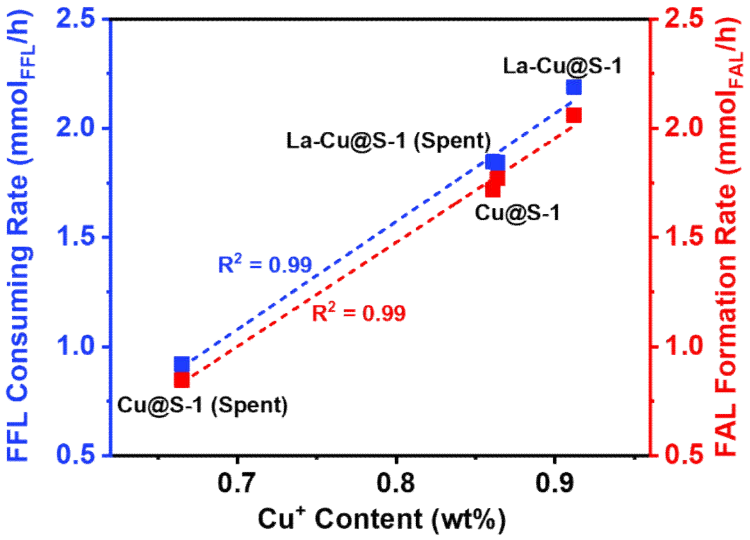

Fig. S11. Correlation between the consuming rate of FFL/formation rate of FAL and the content of Cu^+ in Cu@S-1, La-Cu@S-1, Cu@S-1 (Spent), and La-Cu@S-1 (Spent).

Table S1. Comparison of catalytic performance over the available catalysts for FFL selective hydrogenation to FAL.

Catalyst	Time (h)	T (°C)	P_{H2} (Bar)	Con. (%)	Yield (%)	TOF [$mol_{FAL}/(mol_{Cu}·h)$][a]	Ref.
La-Cu@S-1	3	110	20	99	97.6	66.7	This work
Cu@S-1	3	110	20	87	84.5	54.9	This work
Cu/TS-1	2	110	10	20.3	12.6	7.8	[5]
Cu@TS-1	2	110	10	45.9	34.3	11.4	[5]
Na-Cu/TS-1	2	110	10	72.2	67.2	33.6	[5]
Na-Cu@TS-1	2	110	10	93.0	91.2	55.2	[5]
Cu/CeO_2-R	4	100	20	86.0	83.2	10.5	[6]
Cu/t-ZrO_2-300	4	100	20	100	100	24.2	[7]
Cu/η-Al_2O_3	1	120	10	99.7	93.7	29.3	[8]
Cu/MgO-350	1.3	110	20	99.9	99.9	56.9	[9]
Cu/MgO-La_2O_3	1.17	90	20	>99.9	>99.9	30.7	[10]

[a] The turnover frequency (TOF) was defined as moles of FAL per mol of surface Cu per hour.

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