
Facile Benzene Reduction Promoted by A Synergistically Coupled Cu-Co-Ce Ternary Mixed Oxide

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Experimental

Catalysts preparation

$\text{Cu}_1\text{Co}_5\text{Ce}_5\text{O}_y$ with Cu: Co: Ce atomic ratios equal to 1: 5: 5 was synthesized by co-precipitation method. Appropriate amounts of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (2.171 g), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.242 g) and CoCl_2 (0.649 g) were dissolved in 100 ml deionized water at room temperature and stirred for 15 min, followed by dropwise addition of 100 ml NaOH solution (0.375 M) under vigorous stirring. After stirring for 30 min, the product was dried at 40 °C in vacuum overnight and calcined in air at 600 °C for 1 h with a ramping rate of 1 °C/min.

Reducing $\text{Cu}_1\text{Co}_5\text{Ce}_5\text{O}_y$ was measured under 5 bar H_2 for 0, 6 h, 18 h and 24 h based on the catalytic condition and the sample was named as $\text{Cu}_1\text{Co}_5\text{Ce}_5\text{O}_x$. We do not add any solvent during the $\text{Cu}_1\text{Co}_5\text{Ce}_5\text{O}_y$ pre-treatment process.

Catalysts characterization

The powder X-ray diffraction (XRD) data were recorded with a PANalytical Empyrean diffractometer, operated at 45 kV and 40 mA (scanning step: 0.02 ° per step). The diffraction patterns were recorded in the range of 10–80°.

The N_2 adsorption and desorption isotherms (N_2 -BET) were measured at 77 K under a Micromeritics 3Flex surface area analyzer. Samples were degassed for 12 h under N_2 at 100 °C prior to the measurement.

H_2 temperature program reduction (H_2 -TPR) studies were carried out by Micromeritics AutoChem II 2920 device. The reactor was heated to 750°C at the ramp of 10 °C/min with the hydrogen flow of 30 cm^3 /min. Effluent gas was dried by powder KOH and the consumption of hydrogen were recorded by thermal conductivity detector (TCD).

Elemental analysis of the samples was done by inductively coupled-plasma atomic emission spectroscopy (ICP-AES) using Optima 2100 DV spectrometer (PerkinElmer Corporation), all sample were dissolved in chloroazotic acid and diluted by 1% HNO_3 before ICP measurement.

X-ray photoelectron spectroscopy (XPS) were performed with a PHI 3056 spectrometer equipped with an Al anode source operated at 15 KV and an applied power of 350 W and a pass energy of 93.5 eV. For CuOCoO_yCeO₂ (R), the sample was collected in glovebox and protected by helium (He) in a glass container before the XPS measurement. Finally, the sample was transferred into a UHV chamber, where the XPS experiments were performed.

Diffuse reflectance (DRIFTS) spectra of CO adsorption was obtained on Thermo IS50 FT-IR instrument, scanning 32 scans at the resolution of 4 cm⁻¹. Spectra were presented in the Kubelka-Munk mode and a MCT detector was used. During the in-situ measurement, the sample particles were placed in a 0.56 mm³ micro-reactor, that was mounted in a metal holder. The holder was placed in the beam path of a stainless-steel cell, sealed with KBr windows. First, dried the samples at 100 °C for 30 minutes under an argon atmosphere and cooled to room temperature. An infrared spectrum was obtained and used as a background. The samples were exposed to the CO (50% CO/Ar) for 10-15 min prior to spectra measurement and collected infrared spectra while purged with argon. After that, the sample was then reduced under hydrogen at 100 °C for 24 hours, and above procedures were repeated to obtain the CO-drifts results of reduced samples.

Catalytic hydrogenation of acetyl benzene

0.15 g of substrates, 0.20 g of catalyst was added into 5 mL of hexane in a teflon-lined hydrogenation vessel. Upon sealing, the system was charged to a pressure of 5 bar with H₂ and heated at 100 °C. After the reaction proceeded for the desired period, the reactor was rapidly cooled down to room temperature with an ice bath and the reaction mixture was filtered.

The products were analyzed by a GC-MS system (HP/Agilent 6890GC/5973MSD) equipped with a HP-5MS (30 m × 0.25 mm, film: 0.25 μm) capillary column and FID detector, based on the standard curve. All experiments were performed three times to obtain an average peak area.

$$\text{Conversion (\%)} = \frac{\text{Moles of converted substrates}}{\text{Moles of starting substrates}} \times 100\% \quad (1)$$

$$\text{Yield (\%)} = \frac{\text{Moles of products}}{\text{Moles of starting substrates}} \times 100\% \quad (2)$$

$$\text{TON} = \text{mmol (ethylbenzene)/mmol (active site)}^{1,2} \quad (3)$$

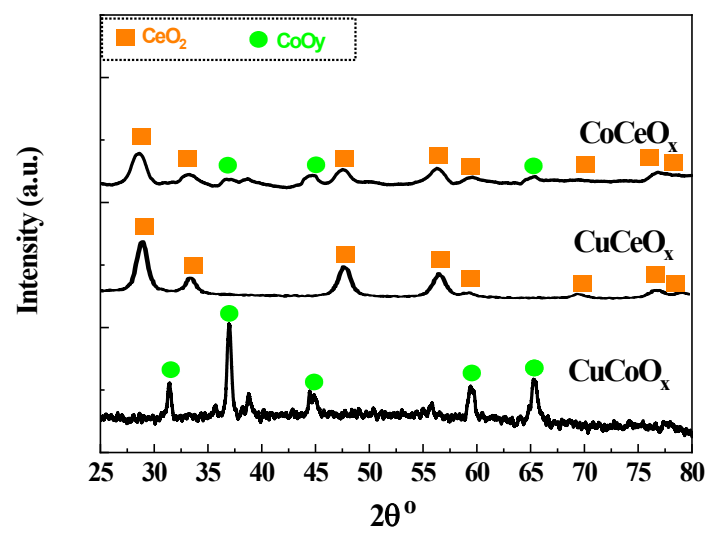


Figure S1. XRD results of CuCoO_x , CuCeO_x and CoCeO_x .

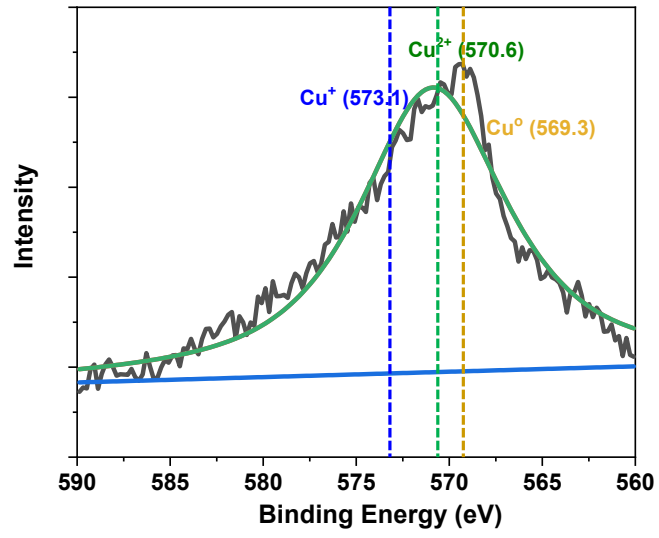


Figure S2. Cu LMM XPS spectra of the Cu₁Co₅Ce₅O_y catalyst.

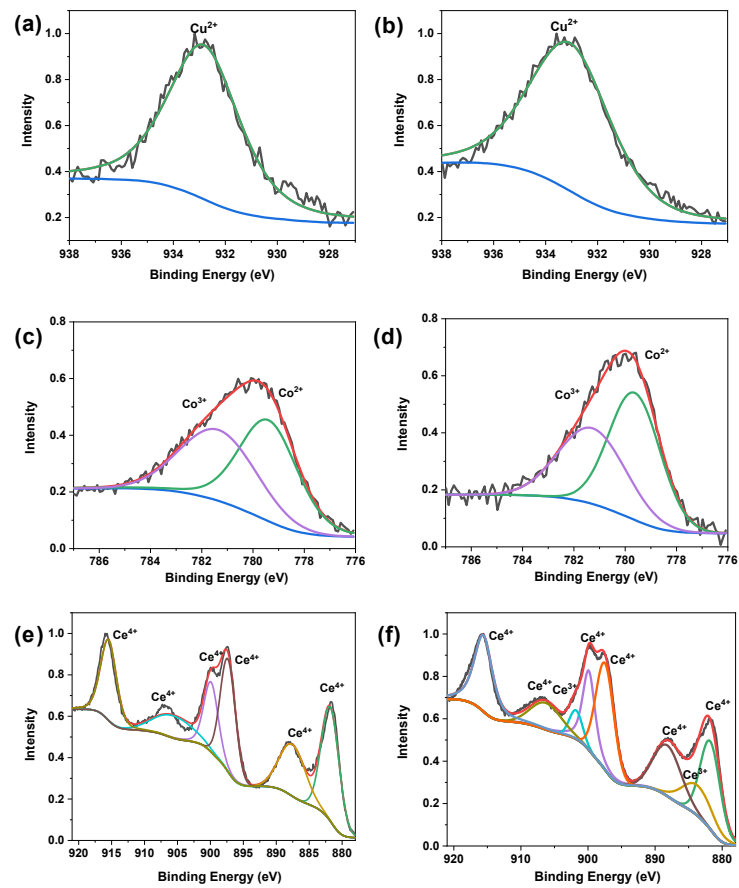


Figure S3 (a), (c) and (e) are XPS results of the Cu, Co and Ce of CuCoCeO_y after pre-treatment of 6 h and (b), (d) and (f) are XPS results of the Cu, Co and Ce of CuCoCeO_y after pre-treatment of 18 h

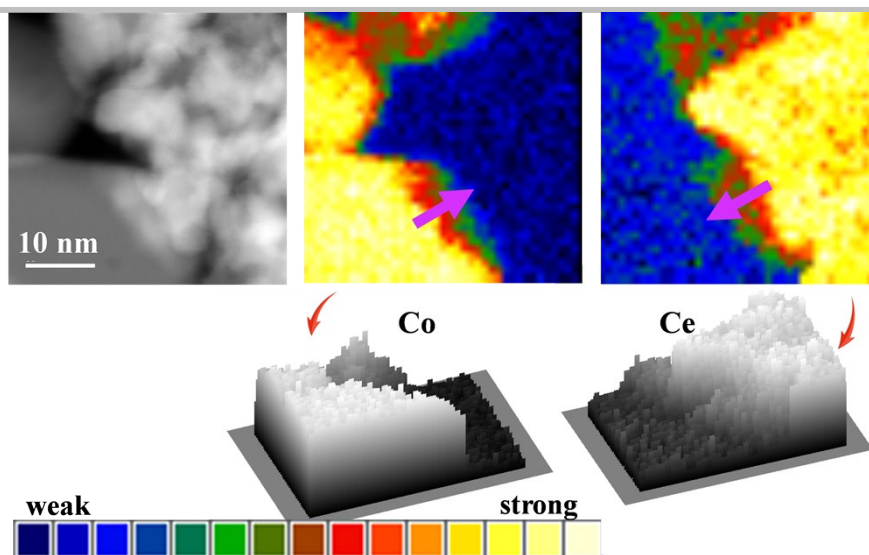


Figure S4. HAADF-STEM images and corresponding EELS elemental maps of $\text{Cu}_1\text{Co}_5\text{Ce}_5\text{O}_y$ catalysts.

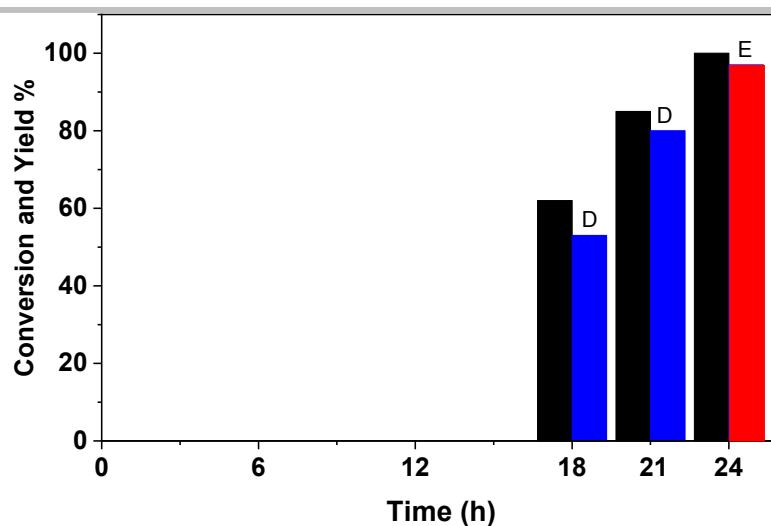


Figure S5. Catalytic hydrodeoxygenation of acetyl benzene over $\text{Cu}_1\text{Co}_5\text{Ce}_5\text{O}_y$ catalyst with different times. Reaction condition: catalyst (100 mg), hexane (5 mL), substrate (1.25 mmol), reaction time (24 h), temperature (100 °C), H_2 (5 bar).

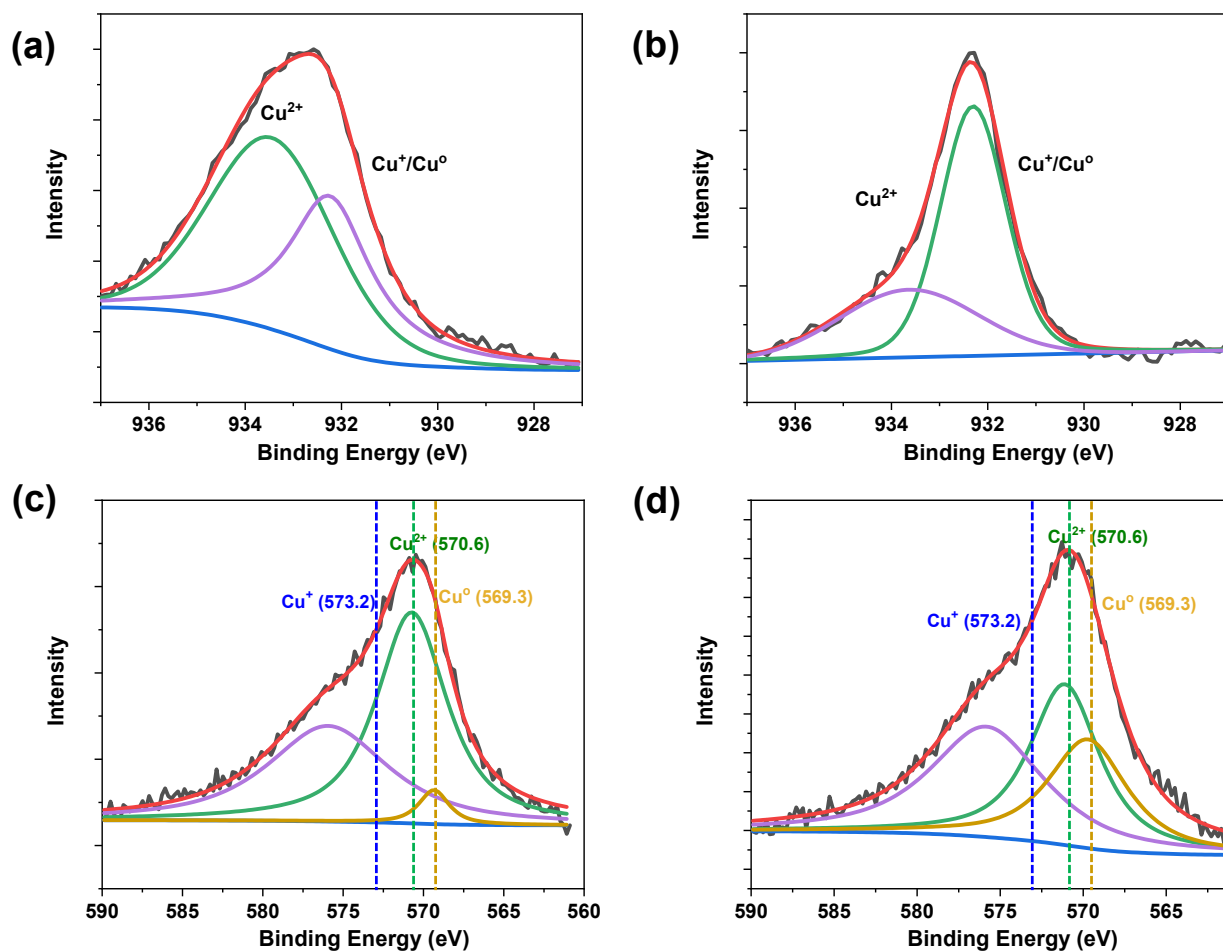


Figure S6. XPS of the Cu in (a) CuCeO_x and (b) CuCoO_x ; Cu LMM XAES spectra of the Cu in (c) CuCeO_x and (d) CuCoO_x .

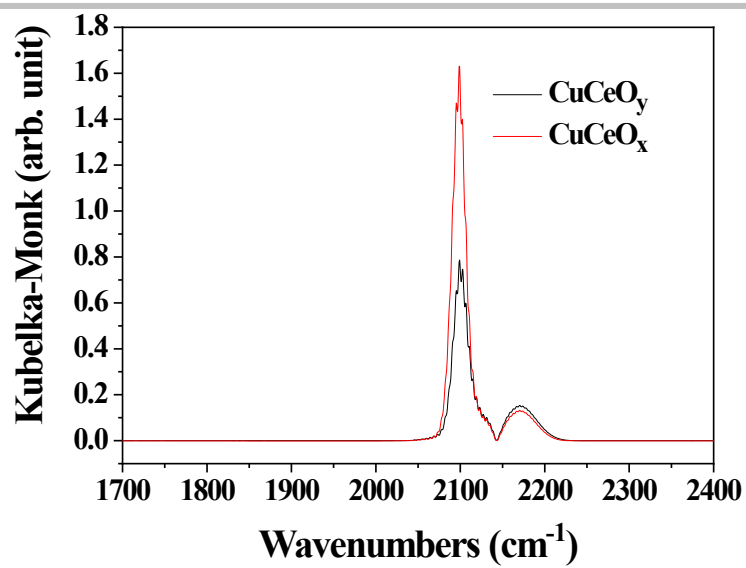


Figure S7. In-situ CODRIFTS of CuCeO_y and CuCeO_x catalysts.

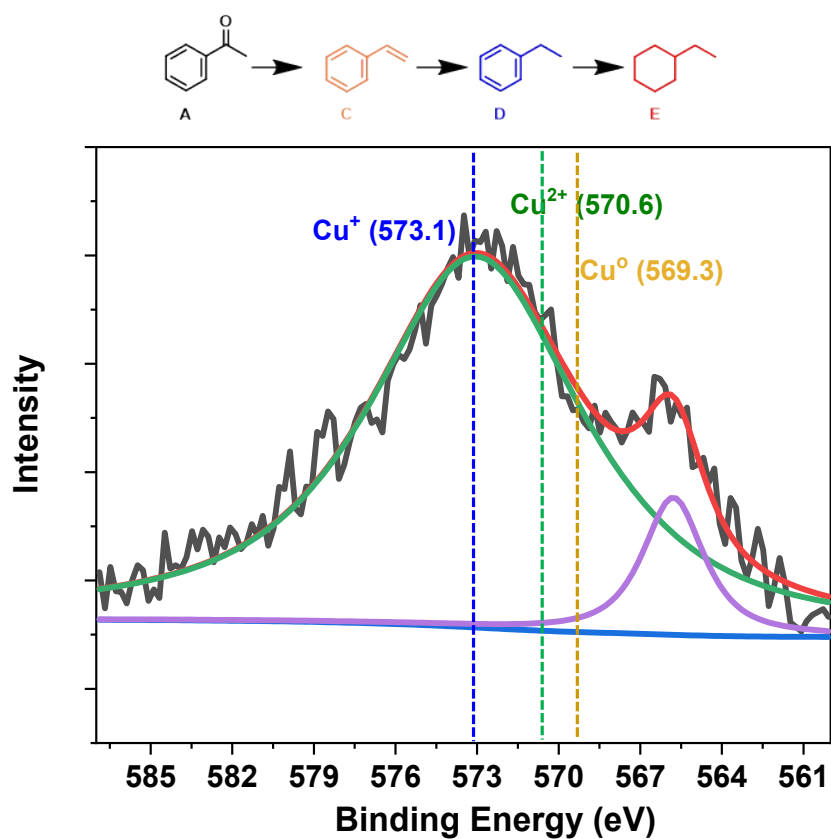


Figure S8. Cu-LMM XPS spectrum of $\text{Cu}_1\text{Co}_5\text{Ce}_5\text{O}_x$ catalyst after recycling for five times.

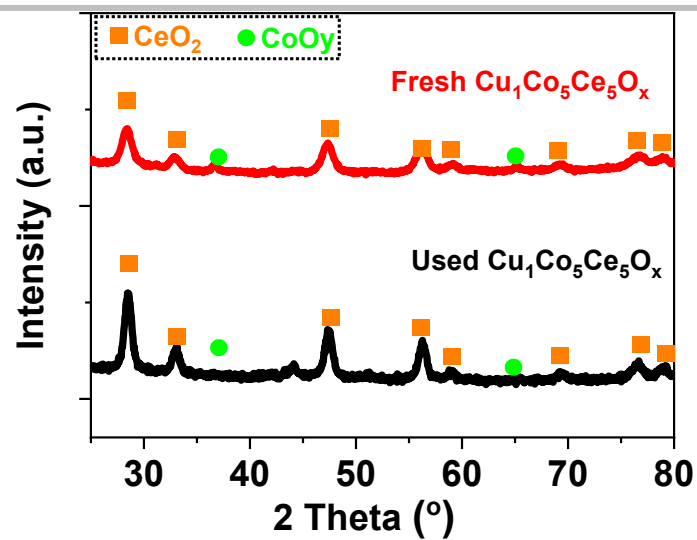


Figure S9. XRD results of the recycled Cu₁Co₅Ce₅O_x catalyst after catalytic use for five times.

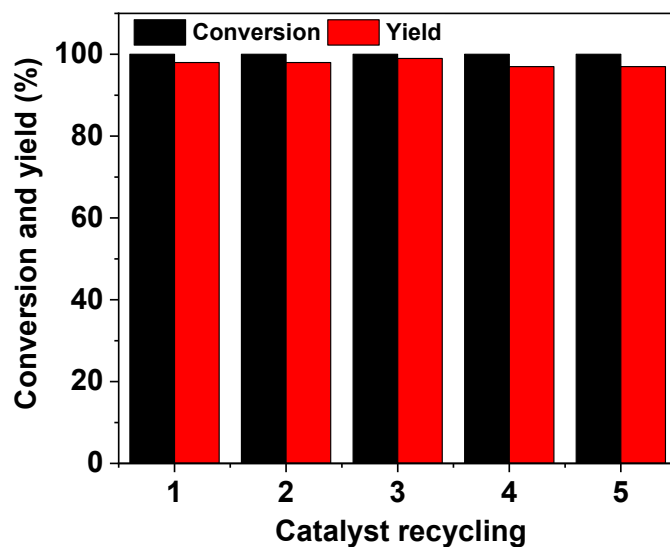


Figure S10. Recycling tests over $\text{Cu}_1\text{Co}_5\text{Ce}_5\text{O}_x$ catalyst in the catalytic hydrodeoxygenation of acetyl benzene. Reaction conditions: $\text{Cu}_1\text{Co}_5\text{Ce}_5\text{O}_x$ (100 mg), hexane (5 mL), substrate (1.25 mmol), reaction time (24 h), temperature (100 °C), H_2 (5 bar)..

Table S1. ICP result of $\text{Cu}_1\text{Co}_5\text{Ce}_5\text{O}_x$ catalyst.

	Cu: Co: Ce ^a	Cu: Co: Ce ^b
$\text{Cu}_1\text{Co}_5\text{Ce}_5\text{O}_x$	1: 5: 5	1: 5: 4

^a Calculated by raw ratio. ^b Calculated by ICP.

Table S2. XPS result of $\text{Cu}_1\text{Co}_5\text{Ce}_5\text{O}_y$ and $\text{Cu}_1\text{Co}_5\text{Ce}_5\text{O}_x$ catalysts.

	Cu^{2+}	$\text{Cu}^{1+}/\text{Cu}^0$	Co^{3+}	Co^{2+}
Binding energy (eV)	933.8	573.2/569.4 ^c	781.2	780.0
$\text{Cu}_1\text{Co}_5\text{Ce}_5\text{O}_y$	100.0	0.0	83.2	16.8
$\text{Cu}_1\text{Co}_5\text{Ce}_5\text{O}_x$	10.0	90.0/0.0	61.9	38.1

^a Calculated by raw ratio. ^b Calculated by ICP. ^c obtained from Cu-LMM measurement.

Reference

1. A. Dubey, L. Nencini, R. R. Fayzullin, C. Nervi and J. R. Khusnutdinova, *ACS Catalysis*, 2017, **7**, 3864-3868.
2. X. Shao, X. Yang, J. Xu, S. Liu, S. Miao, X. Liu, X. Su, H. Duan, Y. Huang and T. Zhang, *Chem*, 2019, **5**, 693-705.