Supporting information

Significantly boosting the production of higher alcohols from biomassderived ethanol utilizing tandem catalysts integrating NiO-modified Cubased component with Mg-Al-Zr mixed metal oxides

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This supporting information contains 22 pages, 7 tables, and 19 figures.

CONENT

Experimental section
Chemicals
Synthesis of reference catalysts
Catalysts characterizations
Figures and tables
Figure S1. (A) XRD patterns of CuNiAl-LDH-x precursors
Figure S2. (A) XRD patterns of MgAlZr-LDH-y precursors. (B) XRD patterns of reduced MgAlZrO
samples
Figure S3. H ₂ -TPR profiles for CuNiAl-MMO samples.
Figure S4. H ₂ -TPR profiles for Cu-NiO-0 MgAlZrO-0.5 and MgAlZrO-0.5 samplesS8
Figure S5. TEM images and the corresponding grain distribution of different reduced Cu-based
samples
Figure S6. Bader charge analysis of Cu-NiO-1 sample based on DFT calculationsS9
Figure S7. (A) Normalized Cu K-edge XANES spectra and (B) Normalized Ni K-edge XANES
spectraS10
Figure S8. (A)XPS of Zr 3d, (B) O 1s, (C) Mg 2p and (D) Al 2p region of MgAlZrO-y samples.
Figure S9. EPR profiles of MgAlZrO-y samplesS11
Figure S10. CO ₂ -TPD profiles (A), corresponding concentration of base sites (B), NH ₃ -TPD profiles
(C), and corresponding concentration of acid sites (D) of Cu-NiO-x catalystsS11
Figure S11. Schematic illustration of the interfacial structure for MgAlZrO componentS12
Figure S12. In-situ DRIFT spectra of ethanol dehydrogenation
Figure S13. Adsorption configurations of reactant and intermediates in the dehydrogenation
pathway in Cu/Al ₂ O ₃ (A) and NiO-Cu/Al ₂ O ₃ (B) modelsS13
Figure S14. The vibrational frequencies of every point in Cu/Al ₂ O ₃ modelsS14
Figure S15. The vibrational frequencies of every point in NiO-Cu/Al ₂ O ₃ modelsS14
Figure S16. The relationship between the ratio of metal/acid-base sites and yield of higher alcohols
in the Cu-NiO-1 MgAlZrO-0.5 composite catalysts with different mass ratioS15
Figure S17. The proposed reaction mechanism for ethanol conversion to n-butanol over Cu-
NiO MgAlZrO composite catalysts
Figure S18. (A) Stability test of Cu-NiO-1 MgAlZrO-0.5 tandem catalysts (mass ratio=1.25:98.75)
in upgrading ethanol to higher alcohols at 275 °C, 2.0 MPa, WHSV 0f 1.42 h ⁻¹ . (B) XRD
patterns of the spent Cu-NiO-1 MgAlZrO-0.5 tandem catalysts. (C) HRTEM images of the
spent Cu-NiO-1 MgAlZrO-0.5 tandem catalysts. (D) XPS spectra of C 1s region for the fresh
and spent Cu-NiO-1 MgAlZrO-0.5 tandem catalysts.
Figure S19. HAADF-STEM image and EDS elemental-mapping analysis of Cu, Ni, Mg, Al, Zr, O,
and C elemental distributions for the spent Cu-NiO-1 MgAlZrO-0.5 tandem catalysts.S16
Table S1. Catalytic performance over different catalysts in the ethanol upgrading
Table S2. Metal contents in different samples.
Table S3. Comparison of Catalytic performance of previously reported various catalysts in the
continuous upgrading of ethanol into higher alcohols in fixed bed reactor
Table S4. The structural data for Cu-based samples. S20

Table S5. Surface acid-basic properties of different Cu-based catalysts	S20
Table S6. Surface acid-basic properties of different MgAlZrO mixed oxide catalysts	S20
Table S7. Ratio of metal/acid-base sites.	S21
References	S21

Experimental Section

Chemicals

All reagents were used without further purification. Analytical Cu(NO₃)₂·3H₂O, Ni(NO₃)₂·6H₂O, Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, Zr(NO₃)₄·5H₂O Na₂CO₃, and NaOH were purchased from Aladdin Reagent Co., Ltd. Anhydrous ethanol (99.9%), Acetaldehyde (99%), ethyl acetate (99.9%), 1-hexanol (> 98.0%), nano-copper oxide and nickel oxide were purchased from Macklin Biochemical CO., Ltd. Pyridine (analytical, 99.5%), 1-butanol (99.5%), and benzene (99.5%) were purchased from J&K Scientific Ltd. Deionized water with an electrical conductivity < 10^{-6} S·cm⁻¹ was used in all experimental processes.

Synthesis of reference catalysts

Cu||MgAlZrO-0.5 component: A certain amount of nano-copper oxide (CuO) and MgAlZrO-0.5 with a mass ratio of 1.25: 98.75, was mixed, grinded, tableted and crushed. Then, the composite reference sample was reduced at 300 °C for 2 h in the flow of 10% H_2 /Ar to obtain the Cu||MgAlZrO-0.5 catalyst.

NiO||**MgAlZrO-0.5 component:** As described in the above procedure, the nickel oxide and MgAlZrO-0.5 with a mass ratio of 1.25: 98.75, was mixed, grinded, tableted, crushed, and reduced in the flow of 10% H_2 /Ar at 300 °C for 2 h. And the obtained sample was denoted as NiO||MgAlZrO-0.5.

NiMgAlZrO component: The reference catalyst (Ni 2.0 wt%) were prepared via a simple impregnation method. The above MgAlZr-LDH-0.5 precursors (1.0 g) were dispersed in 40 mL H₂O, followed by the addition of mixed metal salt solution (10 mL) composed of Ni(NO₃)₂·6H₂O (7.0 mmol/L). After stirring for 1 h, the resultant suspension was heated at 80 °C until the water is completely evaporated. The as-synthesized precipitate was calcined at 550 °C for 6 h and then reduced at 300 °C for 2 h in 10% H₂/Ar atmosphere.

Catalyst characterization

X-ray diffraction (XRD) patterns were recorded from the Rigaku XRD–6000 diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm, 40 kV, 40 mA) at a scanning rate of 10°·min⁻¹. Elemental analysis for Cu-based catalysts was measured by using a Shimadzu ICPS-7500 inductively coupled plasma atomic emission spectroscope (ICP-AES). N₂ adsorption-desorption experiments were performed on a Micromeritics ASAP 200 apparatus, and the specific surface areas were calculated by Brunauer–Emmett–Teller

(BET) methods. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were collected on a JEOL JEM-2100 microscope (accelerating voltage: 200 kV). High-angle annular dark-field scanning transmission electron microscopy (STEM) images were recorded from a JEOL2010F instrument equipped with an energy dispersive X-ray (EDX) spectrometer detector. *Quasi in situ* X-ray photoelectron spectroscopy (XPS) and X-ray excited Auger electron spectra (XAES) were conducted on a Thermo VG ESCALAB250 X-ray photoelectron spectrometer using Al Ka X-ray radiation (hv = 1486.6 eV) with the assistance of the glove box, thus avoiding contact with air during operation. Binding energies were calibrated based on the C1*s* peak at 284.6 eV. Extend X-ray absorption fine structure spectroscopy (EXAFS) at the Cu K-edge was measured at the beamline 1W1B of the Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics (IHEP), and Chinese Academy of Sciences (CAS). Fourier transform of EXAFS spectra were performed in a K-range from 3.0 to 12.8 Å⁻¹. The IFFEFIT 1.2.11 date analysis package (Athena, Artemis, Atoms, and FEFF6) was used for analysis and fitting.

Temperature-programmed reduction of hydrogen (H₂-TPR) was performed on a PCA-1200 instrument equipped with a thermal conductivity detector (TCD). Typically, the catalyst (100 mg) was sealed in a U-shaped quartz tube, pretreated at 200 °C for 60 min under argon flow (40 mL/min), followed by a TPR experiment in a stream of 10% v/v H₂/Ar from 50 °C to 500 °C at a rate of 5 °C/min.

Temperature programmed desorption of NH₃ (NH₃-TPD) and CO₂ (CO₂-TPD) were performed on a PCA-1200. In a typical experiment, the sample (100 mg) was reduced in H₂/Ar atmosphere (10%, v/v; 30 mL/min) at 300°C for 2 h, then switched to a NH₃/CO₂ flow (30 mL/min) at 50 °C for 1 h. After that, the sample was purged with a He flow (30 mL/min) for 1 h to remove physisorbed NH₃/CO₂ and heated from 50 °C to 900 °C at a rate of 10 °C/min.

The metallic copper active surface areas were determined by N₂O titration on a PCA-1200. Typically, the sample (100 mg) was reduced in 10% H₂/Ar flow (40 mL/min) at 300 °C for 2 h, and the H₂ consumption (denoted X) was detected. The gas was switched to N₂O/N₂ (40 mL/min) for 1 h to completely oxidize the surface Cu atoms to Cu₂O species after cooling down to 50 °C in He atmosphere (40 mL/min). The sample was purged with He for 1 h during the cooling process. Subsequently, successive pulses of 10% H₂/Ar (40 mL/min) were introduced at 300 °C to reduce Cu₂O species to metallic Cu. And the amount of consumed hydrogen was detected and denoted as *Y*. The surface area of surface Cu per gram catalyst (S_{Cu} , m²·g_{cat}⁻¹, Eq. 1) was calculated as follows:

$$S = \frac{2 \times N_A \times Y}{1.4 \times 10^{19}}$$
(1)
$$D_{Cu} = \frac{2Y}{X}$$
(2)

Where N_A is the Avogadro's constant, 1.4×10^{19} is the number of copper atoms per square meter.

In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) adsorption experiments were conducted on a Bruker Tensor 27 spectrometer. The samples (30 mg) were placed into the cell, and reduced in 10% H₂/Ar (50 mL/min) at 300 °C for 0.5 h, followed by evacuation at 350 °C for 0.5 h to remove chemisorbed hydrogen. Briefly, the sample was cooled to 50 °C in an Ar flow after the pretreatment, and heated to obtain the background baseline signal from 50 °C to 350 °C. For ethanol/acetaldehyde adsorptiondesorption, the sample was exposed to an ethanol/acetaldehyde flow with Ar as carrier gas (50 mL/min) at 50 °C for 30 min, followed by removing surface physically adsorbed species under Ar flow (50 mL/min) for 10 min. Then, heated up and recorded the spectrum of each temperature point. As for the spectrum of reacting with ethanol/acetaldehyde, the Ar flow with ethanol/acetaldehyde would be purged into the cell at 250 °C for 30 min. And CO-DRIFTS experiments were analogous to the aforementioned process, except for the adsorption temperature which is -70 °C. As for the Pyridine-FTIR spectrum, the samples were mixed with spectrum pure KBr in a ratio of 1:50, then pressed into transparent sheets and installed into an IR cell. Then the background baseline signals were collected after the reduction pretreatment. And the pyridine was injected into the IR cell and kept static adsorption for 10 min at 50 °C. The spectrum was obtained after evacuation for 10 min.





Fig.S1. (A) XRD patterns of CuNiAl-LDH-x precursors: CuNiAl-LDH-0 (a), CuNiAl-LDH-0.5 (b), CuNiAl-LDH-1 (c), and CuNiAl-LDH-1.5 (d). (B) XRD patterns of reduced Cu-NiO samples: Cu-NiO-0 (a), Cu-NiO-0.5 (b), Cu-NiO-1 (c), and Cu-NiO-1.5 (d).



Fig.S2. (A) XRD patterns of MgAlZr-LDH-y precursors: MgAlZr-LDH-0 (a), MgAlZr-LDH-0.1 (b), MgAlZr-LDH-0.25 (c), MgAlZr-LDH-0.5 (d). (B) XRD patterns of reduced MgAlZrO samples: MgAlZrO-0 (a), MgAlZrO-0.1 (b), MgAlZrO-0.25 (c), and MgAlZrO-0.5 (d).



Fig.S3. H₂-TPR profiles for CuNiAl-MMO samples.



Fig.S4. H₂-TPR profiles for Cu-NiO-0||MgAlZrO-0.5 and MgAlZrO-0.5 samples.



Fig. S5. TEM images and the corresponding grain distribution of different reduced Cu-based samples: Cu-NiO-0 (A), Cu-NiO-0.5 (B), Cu-NiO-1 (C), and Cu-NiO-1.5(D).



Fig. S6. Bader charge analysis of Cu-NiO-1 sample based on DFT calculations.



Fig. S7. (A) Normalized Cu K-edge XANES spectra and (B) Normalized Ni K-edge XANES spectra.



Fig. S8. (A)XPS of Zr 3d, (B) O 1s, (C) Mg 2p and (D) Al 2p region of MgAlZrO-y samples: MgAlZrO-0 (a), MgAlZrO-0.1 (b), MgAlZrO-0.25 (c), and MgAlZrO-0.5 (d).



Fig. S9. EPR profiles of MgAlZrO-y samples.



Fig. S10. CO_2 -TPD profiles (A), corresponding concentration of base sites (B), NH₃-TPD profiles (C), and corresponding concentration of acid sites (D) of Cu-NiO-x catalysts: Cu-NiO-0 (a), Cu-NiO-0.5 (b), Cu-NiO-1 (c), and Cu-NiO-1.5 (d).



Fig. S11. Schematic illustration of the interfacial structure for MgAlZrO component.



Fig. S12. *In-situ* DRIFT spectra of ethanol dehydrogenation on Cu||MgAlZrO-0.5 (A), NiO||MgAlZrO-0.5 (B), MgAlZr-0.5 (C), and NiMgAlZr-0.5 (D) versus the reaction time after reduction at 300 °C for 2 h.



Fig. S13. Adsorption configurations of reactant and intermediates in the dehydrogenation pathway in Cu/Al_2O_3 (A) and NiO-Cu/Al_2O_3 (B) models.







1f=3104.452664 cm ⁻¹	15f=1000.028788 cm ⁻¹
2f=3060.446577 cm ⁻¹	16f=843.658277 cm ⁻¹
3f=3021.252422 cm ⁻¹	17f=789.345754 cm ⁻¹
4f=2992.876078 cm ⁻¹	18f=451.078275 cm ⁻¹
5f=2971.004892 cm ⁻¹	19f=382.466902 cm ⁻¹
6f=1449.535389 cm ⁻¹	20f=293.384609 cm ⁻¹
7f=1429.731505 cm ⁻¹	21f=227.554782 cm ⁻¹
8f=1426.565075 cm ⁻¹	22f=159.263686 cm ⁻¹
9f=1346.08497 cm ⁻¹	23f=128.143623 cm ⁻¹
10f=1338.241408 cm ⁻¹	24f=99.870251 cm ⁻¹
11f=1310.894398 cm ⁻¹	25f=80.070174 cm ⁻¹
12f=1238.835635 cm ⁻¹	26f=49.974367 cm ⁻¹
13f=1108.430866 cm ⁻¹	27f/i=73.663713 cm ⁻¹
14f=1078 455571 cm ⁻¹	

1f=3954.139455 cm ⁻¹	15f=860.289039 cm ⁻¹
2f=3234.600836 cm ⁻¹	16f=740.750846 cm ⁻¹
3f=3172.343927 cm ⁻¹	17f=663.667816 cm ⁻¹
4f=3037.389057 cm ⁻¹	18f=472.799478 cm ⁻¹
5f=1957.049791 cm ⁻¹	19f=449.024452 cm ⁻¹
6f=1843.77518 cm ⁻¹	20f=423.198892 cm ⁻¹
7f=1396.502595 cm ⁻¹	21f=352.986476 cm ⁻¹
8f=1389.848882 cm ⁻¹	22f=348.5379 cm ⁻¹
9f=1343.954913 cm ⁻¹	23f=209.563267 cm ⁻¹
10f=1297.484831 cm ⁻¹	24f=189.970464 cm ⁻¹
11f=1113.740925 cm ⁻¹	25f=148.314836 cm ⁻¹
12f=1071.094761 cm ⁻¹	26f=54.939662 cm ⁻¹
13f=1052.717439 cm ⁻¹	27f/i=71.655787 cm ⁻¹
14f=930 886707 cm ⁻¹	

1f=1358.190022 cm ⁻¹
2f=943.229859 cm ⁻¹
3f=681.005801 cm ⁻¹
4f=278.504722 cm ⁻¹
5f=97.383296 cm ⁻¹
6f/i=163.136078 cm ⁻¹

Fig. S14. The vibrational frequencies of every point in Cu/Al_2O_3 models.



15f=994.777725 cm

16f=840.195970 cm

17f=774.615830 cm

18f=435.704563 cm⁻¹

19f=371.371436 cm⁻¹

20f=243.520106 cm⁻

21f=187.040921 cm

22f=160.900113 cm

23f=131.149310 cm⁻¹

24f=128.143623 cm⁻¹

25f=86.226186 cm⁻¹ 26f=51.668219 cm⁻¹

27f/i=78.040921 cm

1f=3156.165469 cm⁻¹

2f=3107.181299 cm

3f=3082.434105 cm

4f=2971.293454 cm

5f=2888.512188 cm

6f=1444.506600 cm⁻¹

7f=1408.089223 cm

8f=1380.479828 cm

9f=1321.272168 cm⁻¹

10f=1299.052023 cm

11f=1236.870153 cm-

12f=1120.025422 cm 13f=1109.506353 cm

14f=1080 665428



1f=3573.770634 cm ⁻¹	15f=885.375994 cm ⁻¹
2f=3261.887176 cm ⁻¹	16f=639.736822 cm ⁻¹
3f=3144.346214 cm ⁻¹	17f=498.007928 cm ⁻¹
4f=3074.553226 cm ⁻¹	18f=481.335848 cm ⁻¹
5f=1530.156363 cm ⁻¹	19f=370.593600 cm ⁻¹
6f=1405.437674 cm ⁻¹	20f=343.280421 cm ⁻¹
7f=1354.128867 cm ⁻¹	21f=272.346903 cm ⁻¹
8f=1338.112275 cm ⁻¹	22f=219.904556 cm ⁻¹
9f=1289.140411 cm ⁻¹	23f=187.187331 cm ⁻¹
10f=1287.285091 cm ⁻¹	24f=154.534989 cm ⁻¹
11f=1197.312379 cm ⁻¹	25f=72.446616 cm ⁻¹
12f=1170.668557 cm ⁻¹	26f=44.826389 cm ⁻¹
13f=1117.941708 cm ⁻¹	27f/i=70.012316 cm ⁻¹
14f=1052.717439 cm ⁻¹	



1f=1487.078059 cm ⁻¹
2f=934.338878 cm ⁻¹
3f=776.486136 cm ⁻¹
4f=257.445468 cm ⁻¹
5f=163.451672 cm ⁻¹
6f/i=172.880137 cm ⁻¹

Fig. S15. The vibrational frequencies of every point in NiO-Cu/Al $_2O_3$ models.



Fig.16. The relationship between the ratio of metal/acid-base sites and yield of higher alcohols over Cu-NiO-1||MgAlZrO-0.5 composite catalysts with different mass ratio.



Figure S17. The proposed reaction mechanism for ethanol conversion to n-butanol over Cu-NiO||MgAlZrO composite catalysts.



Figure S18. (A) Stability and recycling test of Cu-NiO-1||MgAlZrO-0.5 catalyst (mass ratio=1.25:98.75) in upgrading ethanol to higher alcohols at 275 °C, 2.0 MPa, WHSV 0f 1.42 h⁻¹. (B) XRD patterns of the spent Cu-NiO-1||MgAlZrO-0.5 catalyst. (C) HRTEM image of the spent Cu-NiO-1||MgAlZrO-0.5 catalyst. (D) XPS spectra of C 1s region for the fresh and spent Cu-NiO-1||MgAlZrO-0.5 catalyst.



Fig.S19. HAADF-STEM image and EDS elemental-mapping analysis of Cu, Ni, Mg, Al, Zr, O, and C elemental distributions for the spent Cu-NiO-1||MgAlZrO-0.5 catalyst.

Table S1. Catalytic performance over different catalysts in the ethanol upgrading.

	N Select. (%)						STY of C ₄₋₈ OH		
Catalysts	(%)	AcH	EA	BuOH	HexOH	OctOH	C ₄₋₈ OH	Others ^b	(mol·mol _{Cu0} ⁻¹ ·h ⁻¹
Cu-NiO-0 MgAlZrO-0	17.1	26.9	17.6	42.3	10.2	0	52.5	3	332.3
Cu-NiO-0 MgAlZrO-0.1	16.6	35.8	18.0	38.3	4.2	0	42.3	3.7	320.5
Cu-NiO-0 MgAlZrO-0.25	32.7	38.7	10.0	42.0	5.0	0	47.0	4.3	569.7
Cu-NiO-0 MgAlZrO-0.5	27.6	17.8	12.6	65.3	2.9	0.2	68.4	1.2	688.4
Cu-NiO-0.5 MgAlZrO-0.5	42.9	13.6	8.2	58.7	5.2	0	63.9	14.3	1203.5
Cu-NiO-1 MgAlZrO-0	21.7	28.3	16.7	37.9	6.6	0	44.5	10.5	643.4
Cu-NiO-1 MgAlZrO-0.1	33.4	26.7	11.2	35.2	7.3	0	42.5	19.6	943.7
Cu-NiO-1 MgAlZrO-0.25	46.3	20.6	5.8	40.1	8.9	0	49.0	24.6	1501.3
Cu-NiO-1 MgAlZrO-0.5	64.6	1.5	1.9	29.5	36.1	5.7	71.3	25.3	3045.6
Cu-NiO-1.5 MgAlZrO-0.5	43.7	6.7	5.0	31.8	30.1	7.4	69.3	19.0	2402.5
Cu MgAlZrO-0.5	10.7	18.9	25.6	37.9	6.5	0.5	44.9	10.6	-
NiO MgAlZrO-0.5	2.2	5.3	35.1	40.7	8.6	1.2	50.5	9.1	-
NiMgAlZrO-0.5	4.5	7.8	27.8	45.2	12.8	3.7	61.7	2.7	-
Cu-NiO-1 MgAlZrO-0.5 d	68.2	2.0	2.7	38.4	31.7	5.0	75.1	20.2	3388.7
Cu-NiO-1 MgAlZrO-0.5 °	72.4	53.2	15.8	23.7	0	0	23.7	7.3	-
Cu-NiO-1 MgAlZrO-0.5 f	30.4	3.4	5.7	47.0	24.3	8.2	79.5	11.4	-

[a] Reaction conditions: tandem catalysts 1.0 g (1.25: 98.75 by mass ratio of Cu-NiO-x/MgAlZrO-y), 250 °C, WHSV of 1.42 h⁻¹, N₂ (2 MPa, 30 mL/min); [b] Other products include butyl acetate, ethyl butyrate, 1,1-diethoxyethane, 2-ethyl-butanol, 2-ethyl hexanal etc. [c] STY of C₄₋₈OH represents the space time yield of higher alcohols based on the moles of surface metallic copper sites in the tandem catalysts. [d] Reaction conditions: tandem catalysts 1.0 g (1.25: 98.75 by mass ratio of Cu-NiO-x/MgAlZrO-y), 275 °C, WHSV of 1.42 h⁻¹, N₂ (2.0 MPa, 30 mL/min). [e] Reaction conditions: tandem catalysts 1.0 g (1.25: 98.75 by mass ratio of Cu-NiO-1/MgAlZrO-y), 275 °C, WHSV of 1.42 h⁻¹, N₂ (0.1 MPa, 30 mL/min). [f] Reaction conditions: tandem catalysts 1.0 g (1.25: 98.75 by mass ratio of Cu-NiO-1/MgAlZrO-0.5), 250 °C, WHSV of 1.42 h⁻¹, N₂ (0.1 MPa, 30 mL/min). [f] Reaction conditions: tandem catalysts 1.0 g (1.25: 98.75 by mass ratio of Cu-NiO-1/MgAlZrO-0.5), 250 °C, WHSV of 1.42 h⁻¹, N₂ (0.1 MPa, 30 mL/min). [f] Reaction conditions: tandem catalysts 1.0 g (1.25: 98.75 by mass ratio of Cu-NiO-1/MgAlZrO-0.5), 250 °C, WHSV of 1.42 h⁻¹, N₂ (0.1 MPa, 30 mL/min). [f] Reaction conditions: tandem catalysts 1.0 g (1.25: 98.75 by mass ratio of Cu-NiO-1/MgAlZrO-0.5), 250 °C, WHSV of 1.42 h⁻¹, N₂ (0.1 MPa, 30 mL/min). [f] Reaction conditions: tandem catalysts 1.0 g (1.25: 98.75 by mass ratio of Cu-NiO-1/MgAlZrO-0.5), 250 °C, WHSV of 1.42 h⁻¹, N₂ (4 MPa, 30 mL/min).

	Content	(wt.%)
Catalysts	Cu	Ni
Cu-NiO-0 ^a	46.50	0
Cu-NiO-0.5 ^a	40.80	11.00
Cu-NiO-1 ^a	35.70	18.80
Cu-NiO-1.5 ^a	32.10	24.80
Cu-NiO-0 MgAlZrO-0.5 (1.25:98.75) b	0.58	0
Cu-NiO-0.5 MgAlZrO-0.5 (1.25:98.75) ^b	0.51	0.14
Cu-NiO-1 MgAlZrO-0.5 (1.25:98.75) b	0.45	0.24
Cu-NiO-1.5 MgAlZrO-0.5 (1.25:98.75) b	0.40	0.31
Cu-NiO-1 MgAlZrO-0.5 (5:95) b	1.79	0.94
Cu-NiO-1 MgAlZrO-0.5 (10:90) ^b	3.57	1.88
Cu-NiO-1 MgAlZrO-0.5 (20:80) ^b	7.14	3.76

Table S2. Metal contents in different samples.

[a] Metal content was determined by ICP-AES analysis. [b] Metal content was determined by the measured metal content of Cu-NiO samples by ICP-AES and the actual mass ratio of Cu-NiO component in composite catalysts.

C-t-1 t	Reaction conditions	Conv.	Select. ^a	Yield. ^b	STY of C ₄₋₈ OH $^\circ$	D.C
Catalysts	in fixed bed reactor	(%)	(%)	(%)	$(\text{mmol} \cdot g_{\text{metal}} \cdot 1 \cdot h^{-1})$	Refs
Pd@UiO-66	250 °C, 2 MPa, LHSV=4 mL/(h·g _{cat})	49.9	50.1	25.0	17.1	[1]
Ru/Mg ₃ AlO _x	350 °C, 0.1 MPa, WHSV=3.2 h ⁻¹	29.6	82.6	24.4	17.0	[2]
Ag/Mg ₂ AlO _x	350 °C, 0.1 MPa, LHSV=6 mL/(h·g _{cat})	23.3	77.0	17.9	18.5	[3]
Pd-CeO ₂ /AC	250 °C, 2 MPa, LHSV=4 mL/($h \cdot g_{cat}$)	11.9	67.6	8.0	5.5	[4]
Co-CeO ₂ /AC	250 °C, 2 MPa, LHSV=4 mL/($h \cdot g_{cat}$)	34.1	47.6	16.2	11.1	[4]
Ni-CeO ₂ /AC	250 °C, 2 MPa, LHSV=4 mL/($h \cdot g_{cat}$)	31.6	50.6	16	11.0	[4]
Co-MgAlO _x	250 °C, 0.1 MPa, 0.96 g·g _{cat} ⁻¹ ·h ⁻¹	32.9	95.4	31.4	6.4	[5]
Cu-CeO ₂ /AC	250 °C, 2 MPa, LHSV=2 h ⁻¹	45.6	42.4	19.3	13.3	[6]
Cu-CeO ₂ /SiO ₂	250 °C, 2 MPa, LHSV=2 h ⁻¹	23.3	10.2	2.4	1.6	[6]
Cu-CeO ₂ /Al ₂ O ₃	250 °C, 2 MPa, LHSV=2 h ⁻¹	46.9	12.1	5.7	3.9	[6]
Ni-MgAlO _x	250 °C, 3 MPa, WHSV=3.2 h ⁻¹	18.7	85	15.9	11	[7]
NiO-Cu-LaAlO _x	250 °C, 3 MPa, LHSV=2 mL/($h \cdot g_{cat}$)	56.7	76.1	43.1	14.8	[8]
Cu-NiMgAl	250 °C, 3 MPa, WHSV=1.69 h ⁻¹	30	64.2	19.3	7.1	[9]
CuLaAlO _x	260 °C, 3 MPa, LHSV=2 mL/($h \cdot g_{cat}$)	52.5	72.7	38.2	12.9	[10]
Cu/HSACeO ₂	260 °C, 10 MPa, LHSV=1.97 h ⁻¹	67	44.8	30.0	12.9	[11]
Pt-Y/Beta	200 °C, 0.1 MPa, WHSV=2.0 h ⁻¹	34	68	23.1	15.1	[12]
0.3wt%Cu/Mg2.9AlO	325 °C, 2.1 MPa, WHSV=1.3 h ⁻¹	68.4	40.9	28.0	7.9	[13]
0.3wt%CuMMO	325 °C, 2.1 MPa, WHSV=6.56 h ⁻¹	51	57	29.1	41.5	[14]
НАР	325 °C, 520 s·kg _{HAP} ·mol _{alcohol} ⁻¹	11.9	89.3	10.6	-	[15]
0.1wt%Cu/MgAlO	325 °C, 4.2 MPa H ₂ , WHSV=0.2 h ⁻¹	65	75	48.8	2.1	[16]
Cu-NiO-1 MgAlZrO-0.5	250 °C, 2 MPa, WHSV=1.42 h ⁻¹	68.2	75.1	51.2	15.8	This work

Table S3. Comparison of Catalytic performance of previously reported various catalysts in the continuous upgrading of ethanol into higher alcohols in fixed bed reactor.

[a] The products include n-BuOH, HexOH and OctOH. [b] Yield represents the yield of higher alcohols.

[c] STY of C₄₋₈OH represents the space time yield of higher alcohols based on the weight of catalyst.

Table S4. The structural data for Cu-based samples.

	$D_{\mathrm{Cu}}{}^{\mathrm{a}}$	Surface Cu ⁰	Surface Cu ^{+ b}	H ₂ consumption	Reduction degree	
Catalysts	(0/)	(µmol/g)	(µmol/g)	(mmol/g)	copper ^d	
	(%)				(%)	
Cu-NiO-0	15.4	674	317	4.38	59.9	
Cu-NiO-0.5	20.5	565	271	2.76	43.1	
Cu-NiO-1	22.7	373	213	1.65	29.4	
Cu-NiO-1.5	16.8	313	157	1.86	36.9	
spent-Cu-NiO-1	18.2	-	-	-	-	

[a] Determined by N₂O titration. [b] Deduced from metallic copper surface area and Cu XAES results. [c-d] Calculated by the results of H₂-TPR experiments. [e] After reaction of 50 h at 275 °C, 2 Mpa.

Table S5. Surface acid-basic properties of different Cu-based catalysts.

Catalanta	Acid Sites (µmol • g ⁻¹)			Base Sites (µmol • g ⁻¹)					
Catalysis -		$A_{NH3}{}^{a} \\$	$A_W{}^b$	A_{MS}	$A_S{}^d$	$B_{CO2}{}^{\mathfrak{c}}$	$\mathbf{B}_{W}^{\mathrm{f}}$	$B_{MS}{}^{g} \\$	\mathbf{B}_{S}^{h}
	Cu-NiO-0	529.1	177.7	242.(108.8	123.4	74.3	31.0	18.2
	Cu-NiO-0.5	169.8	58.0	50.8	61.0	127.1	68.3	31.2	27.6
	Cu-NiO-1	173.6	39.8	75.4	58.4	144.3	73.4	39.5	31.4
	Cu-NiO-1.5	335.0	106.5	116.9	111.6	133.2	72.3	38.6	22.3

[a] The total concentration of acid sites calculated from NH₃-TPD in the region of 50–500 °C. [b-d] A_W , A_{MS} , and A_S are the concentration of weak, medium-strong, and strong acid sites, respectively, based on the deconvoluted TPD profiles. [e] The total concentration of base sites calculated from CO₂-TPD in the region of 50–500 °C. [f-h] B_W , B_{MS} , and B_S are the concentration of weak, medium-strong, and strong base sites, respectively, on the basis of deconvoluted CO₂-TPD profiles.

Table S6. Surface acid-basic properties of different MgAlZrO mixed oxide catalysts.

Catalysts —	Acid Sites (µmol • g ⁻¹)			Base Sites (µmol • g ⁻¹)		
	$A_{NH3}{}^{a} \\$	$A_W{}^b$	A _S ^c	$\mathbf{B}_{\mathrm{CO2}}^{\mathrm{d}}$	$B_{W}{}^{e}$	$\mathbf{B}_{\mathbf{S}}^{\mathbf{f}}$
MgAlZrO-0	262.5	35.9	226.6	256.6	78.4	178.2
MgAlZrO-0.1	426.7	43.2	383.5	365.8	91.2	274.6
MgAlZrO-0.25	503.7	46.3	457.4	391.3	123.	267.4
MgAlZrO-0.5	539.8	42.9	496.9	353.0	200.	152.1

[a] The total concentration of acid sites calculated from NH₃-TPD in the region of 50–550 °C. [b-c] A_W and A_S are the concentration of weak, and strong acid sites, respectively, based on the deconvoluted TPD profiles. [d] The total concentration of base sites calculated from CO₂-TPD in the region of 50–550 °C. [e-f] B_W and B_S are the concentration of weak and strong base sites, respectively, on the basis of deconvoluted CO₂-TPD profiles.

		Ratio ^a			
Catalysts	Mass ratio	Metal /acid sites	Metal/base sites	Acid/base sites	
Cu-NiO-1 MgAlZrO-0.5	0:100	0.00	0.00	1.53	
Cu-NiO-1 MgAlZrO-0.5	1.25:98.75	0.01	0.01	1.53	
Cu-NiO-1 MgAlZrO-0.5	5:95	0.04	0.05	1.52	
Cu-NiO-1.5 MgAlZrO-0.5	10:90	0.07	0.11	1.52	
Cu-NiO-1 MgAlZrO-0.5	20:80	0.16	0.24	1.50	
Cu-NiO-1 MgAlZrO-0.5	100:0	2.15	2.58	1.20	

 Table S7. Ratio of metal/acid-base sites.

[a] The density of metallic copper sites is based on N₂O titration.

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