Supporting Information

Synergistic Effects of Oxygen Vacancies and Metal-Support Interaction in Rare Earth-Modified Cu-ZnO-Al_2O_3 Catalysts for CO_2 Hydrogenation to Methanol

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Characterization of catalysts

Powder X-ray diffraction (XRD) was conducted using a DX2700 apparatus with Cu Kα radiation. The range of 2θ is from 10 ° to 90 °, with a step increment of 0.02 °. All catalysts underwent pretreatment at 300 °C under 10 vol% H_2/N_2 for an hour prior to testing.

The Brunauer-Emmett-Teller (BET) specific surface area and pore size distribution were determined from the nitrogen adsorption-desorption isotherms at -196 °C using a V-Sorb-2802TP instrument. All catalysts were pretreated at 300 °C for 1 hour in a 10 vol% H_2/N_2, and the reduced samples were degassed at 200 °C for 6 hours to clean the surface prior to the measurement. The specific surface area was calculated by fitting the Brunauer-Emmett-Teller (BET) equation, whereas the pore size and pore volume were determined using the Barrett-Joyner-Halenda (BJH) model.

Analysis using a transmission electron microscope (TEM) and the EDX mapping analyses was conducted on the Talos F200S. All catalysts required pretreatment at 300 °C for an hour under 10 vol% H_2/N_2. The statistical Cu particle size of the sample was determined using Nano Measurer software.

Spectroscopy (XPS) was recorded on a Thermo ESCALAB -250XI (16KV 14.9mA) with Al Kα radiation. All catalysts were pre-treated at 300 °C for 1 h under 10 vol% H_2/N_2.

Carbon dioxide temperature-programmed desorption (CO_2-TPD) and hydrogen temperature-programmed reduction (H_2-TPR) experiments were both carried out in a quartz U-tube reactor, using a Xian quan TP5076 automatic adsorption instrument. For CO_2-TPD measurements: 100 mg of calcined sample was in-situ reduced at 300 °C for 60 min with a flowing 10 vol% H_2/N_2 (flow rate: 40 mL min^{-1}). After the sample was cooled to room temperature, it was exposed to a CO_2 stream (flow rate: 40 mL min^{-1}) until adsorption saturation, followed by purging with high-purity helium (He) for 30 min to flatten the baseline. The TPD test was performed in the temperature range of 30-900 °C at a heating rate of 10 °C min^{-1}, with He serving as the carrier gas throughout the process. For H_2-TPR measurements: 50 mg of calcined sample was in-situ pretreated at 300 °C for 60 min with a flowing N_2 stream (flow rate: 40 mL min^{-1}). After the pretreatment was completed and the sample was cooled to room temperature, a 10 vol% H_2/N_2 mixture was introduced, and data recording was initiated simultaneously while heating to 500 °C at a rate of 10 °C min^{-1}.

In-situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTs) was performed on a Bruker INVENIO SFTIR equipped with a mercury-cadmium-telluride (MCT) detector following the procedure described below. The test was conducted with a spectral resolution of 4 cm^{-1} and a scanning range of 800-4000 cm^{-1} to evaluate the surface intermediate species during CO_2 adsorption and hydrogenation. Prior to the test, 50 mg of unreduced catalyst was In-situ reduced at 300 °C for 1 h in a 10 vol% H_2/N_2 atmosphere with a flow rate of 30 mL min^{-1}. Subsequently, the catalyst was purged with N_2 for 30 min to remove physically adsorbed H_2, then cooled to 220 °C, and the background spectrum was collected. Finally, the N_2 was replaced with the feed gas mixture (CO_2/H_2 = 1/3), and the time-dependent evolution of intermediate products was recorded to obtain infrared spectra with a resolution of 4 cm^{-1}. Meanwhile，After the same pretreatment procedure described above, in-situ CO_2 adsorption DRIFTs tests were performed by introducing pure CO_2 into the reaction chamber. The dynamic evolution of surface adsorbed species and reaction intermediates was continuously recorded to clarify the CO_2 activation pathway over the catalyst surface.

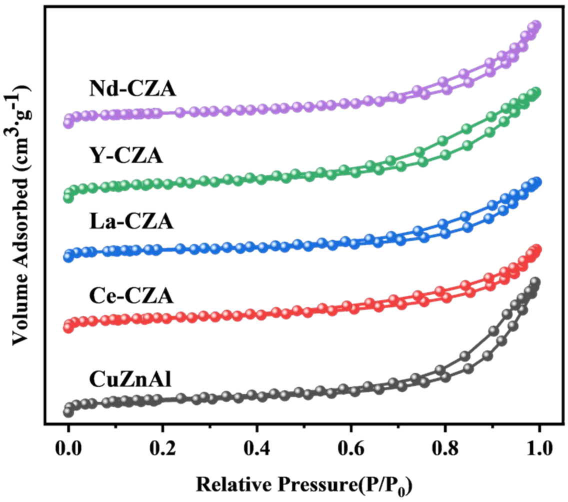

Fig. S1 The N_2 adsorption-desorption curves of the reduced CuZnAl and RE-CZA catalysts.

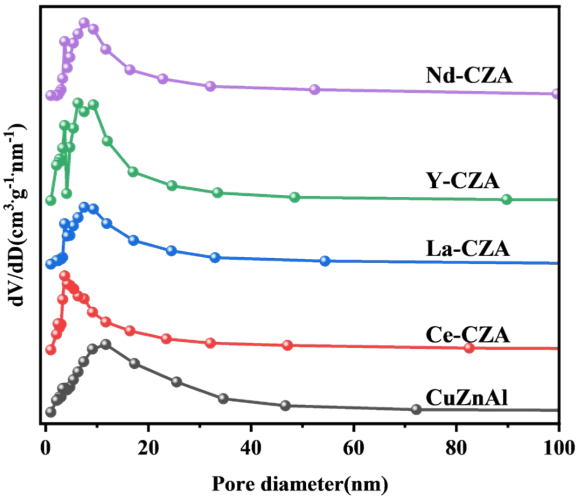

Fig. S2 The pore size distribution curves of the reduced CuZnAl and RE-CZA catalysts.

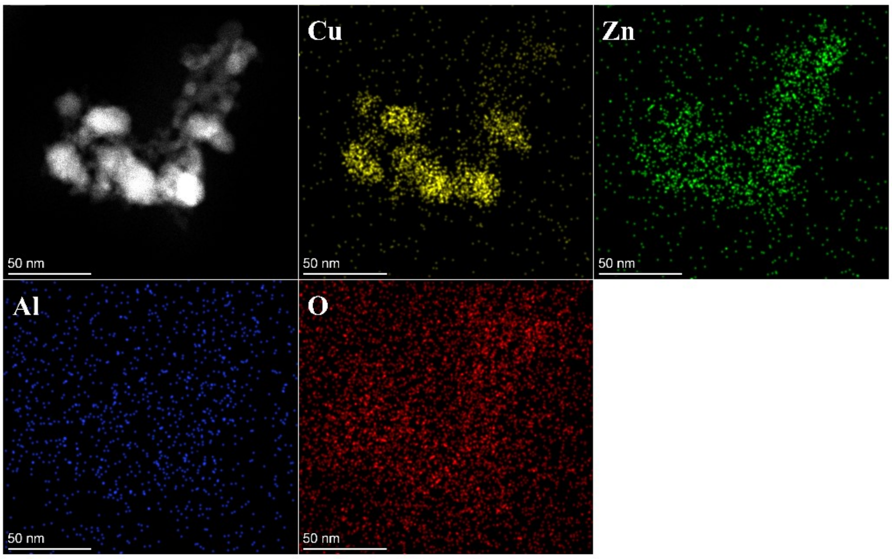

Fig. S3 HAADF-STEM and corresponding element mapping of CuZnAl catalyst.

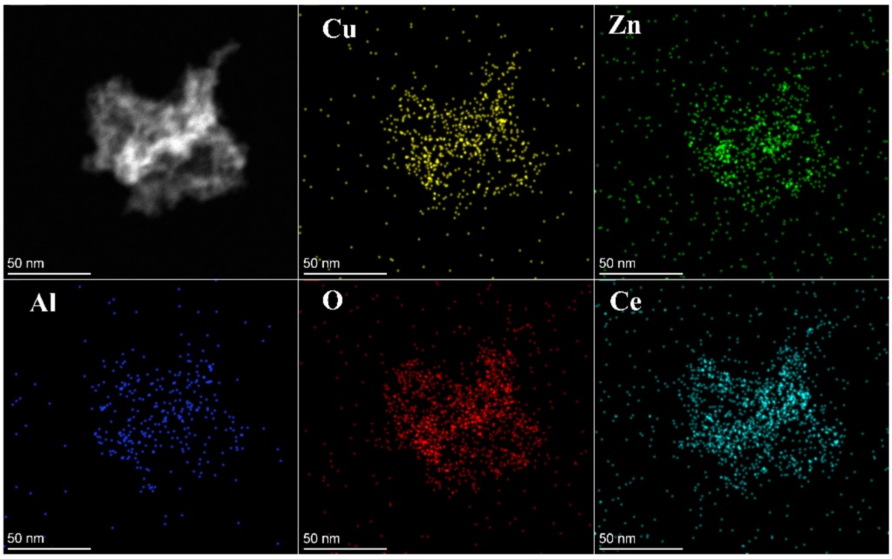

Fig. S4 HAADF-STEM and corresponding element mapping of Ce-CZA catalyst.

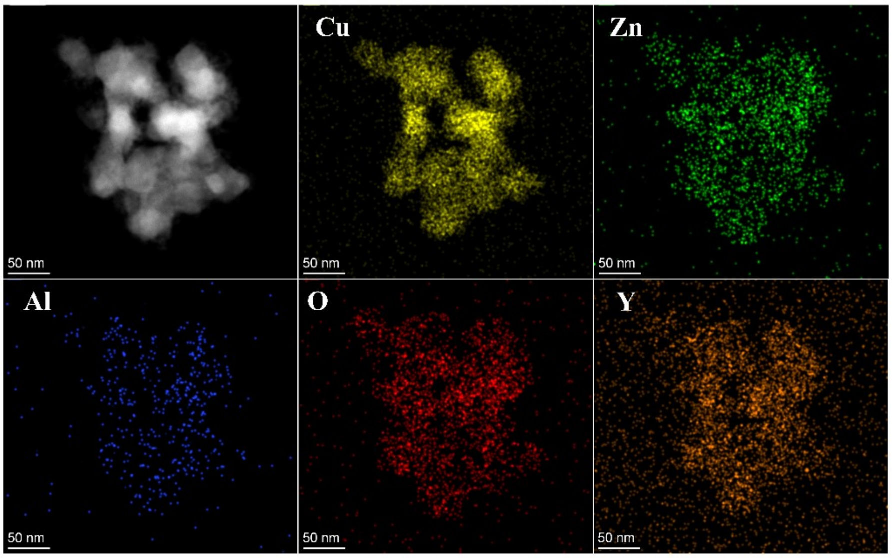

Fig. S5 HAADF-STEM and corresponding element mapping of Y-CZA catalyst.

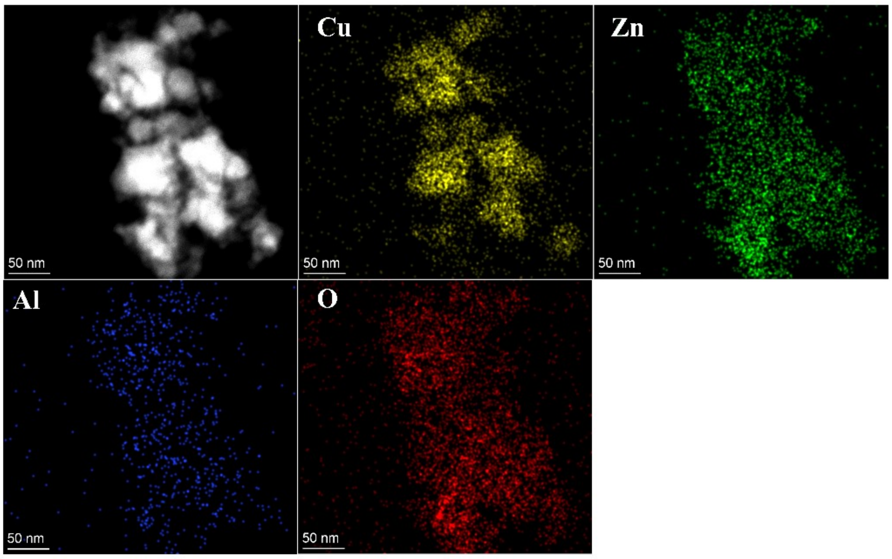

Fig. S6 HAADF-STEM and corresponding element mapping of the spent CuZnAl.

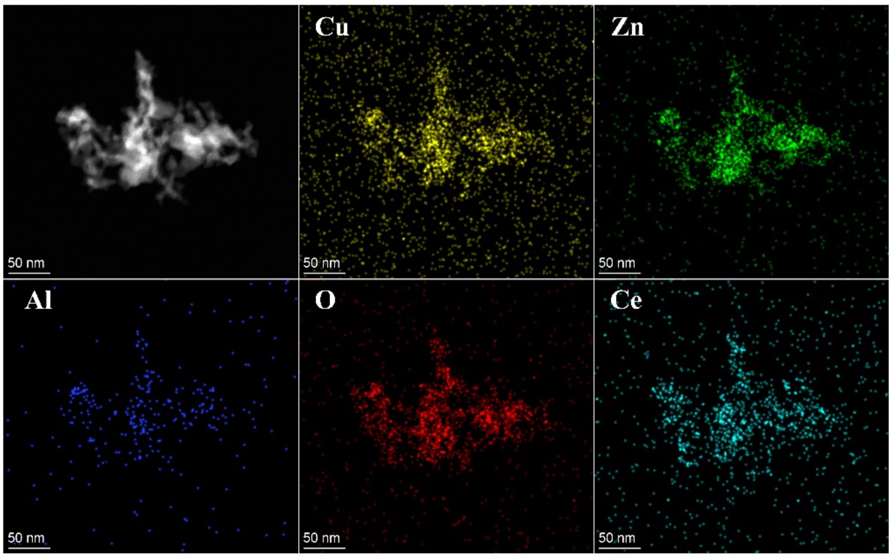

Fig. S7 HAADF-STEM and corresponding element mapping of the spent Ce-CZA catalyst.

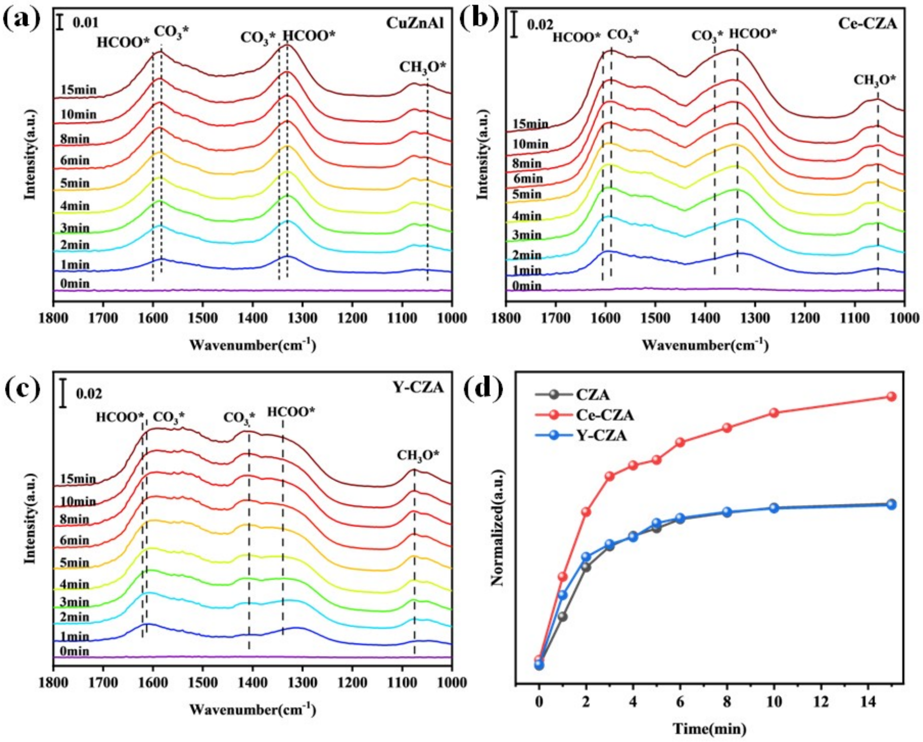

Fig. S8 (a-c) In-situ DRIFTs for CO$_2$ adsorption: CuZnAl, Ce-CZA and Y-CZA (c) Normalization of the peak area of HCOO*.

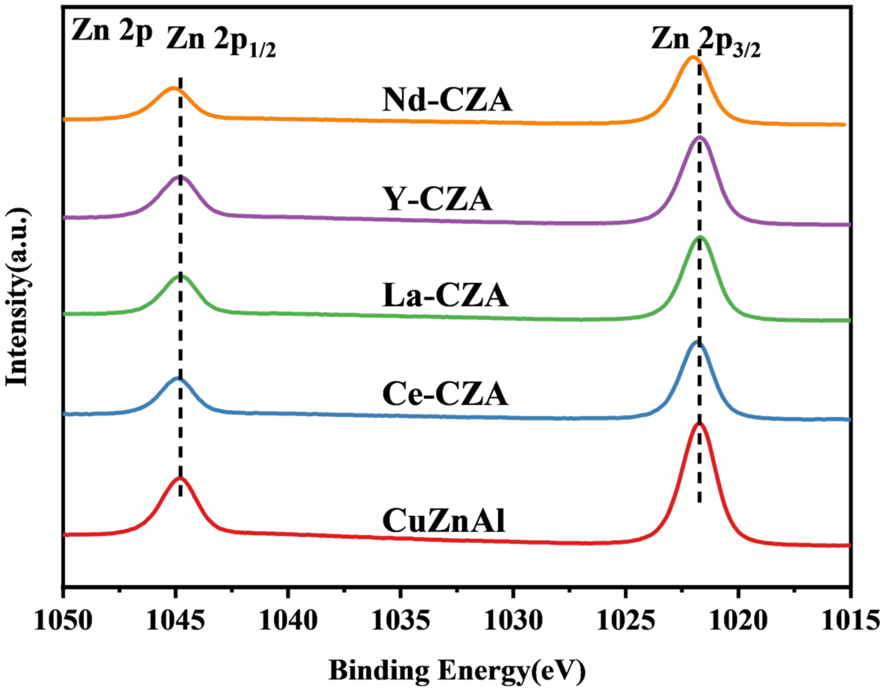

Fig. S9 Zn 2p spectra of the reduced CuZnAl and RE-CZA catalysts.

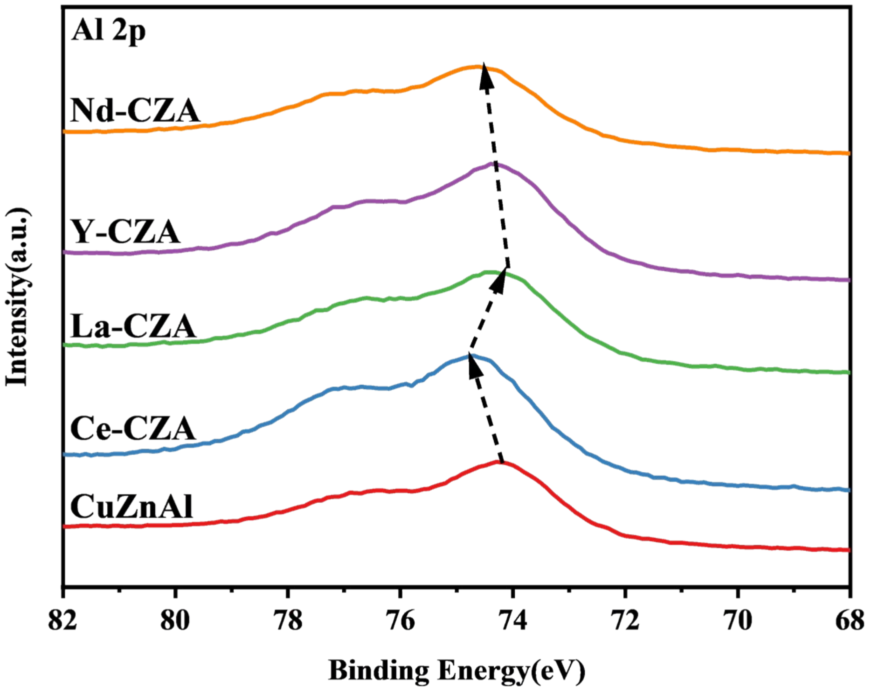

Fig. S10 Al 2p spectra of the reduced CuZnAl and RE-CZA catalysts.

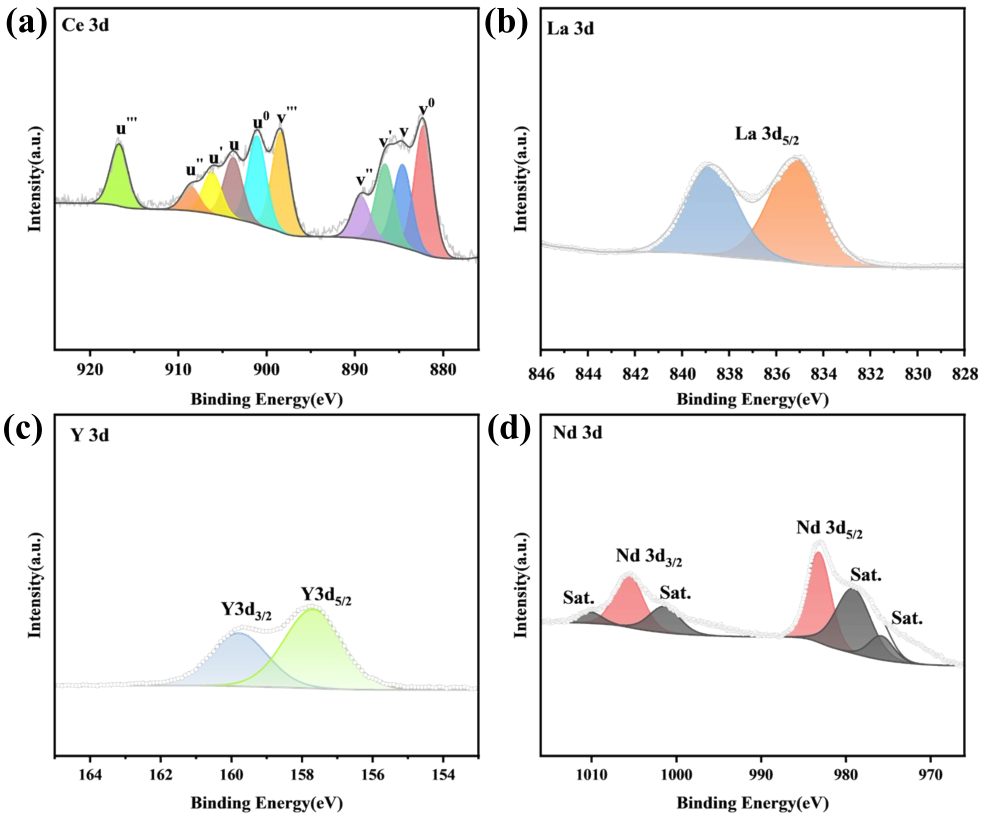

Fig. S11 RE 3d spectra of the reduced RE-CZA catalysts. (a)Ce 3d (b)La 3d (c)Y 3d (d)Nd 3d.

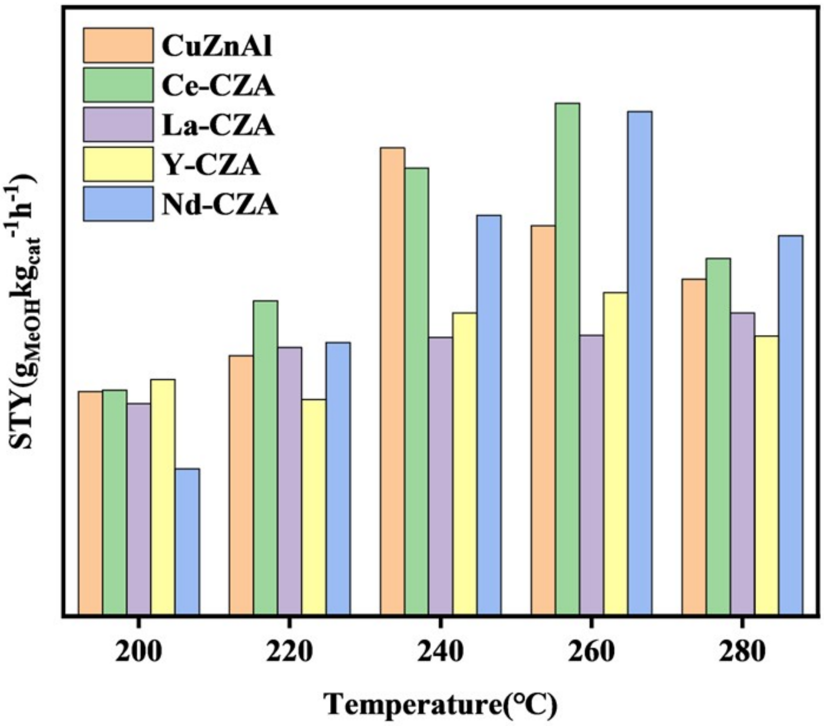

Fig. S12 Methanol space-time yield of CuZnAl and RE-CZA catalysts in the range of 200-280 °C.

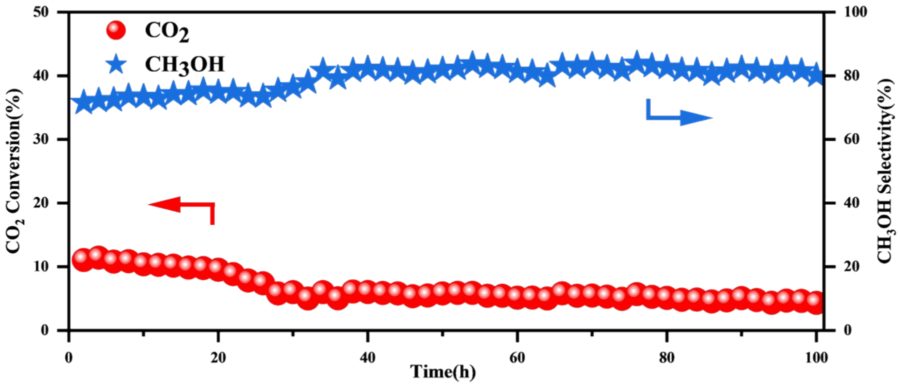

Fig. S13 Long-term stability of the Ce-CZA catalyst.