Supporting Information

Oxygen Vacancies Enriched MOF-derived Mn₂O₃ Catalysts for High-Efficiency Direct Synthesis of Ethylene Urea from CO₂

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Catalyst characterization

A D/MAX2500/PC powder diffractometer (Rigaku) with Cu K α radiation source was operated at 40 kV and 200 mA to record the X-ray Diffraction (XRD) patterns in reflection geometry to identify the crystalline structure of samples.

Transmission Electron Microscope (TEM) was conducted using a Philips Tecnai G2 F20 microscope operated at 300 kV. Energy dispersive X-ray spectroscopy (EDS) and corresponding elemental maps was collected through a high-resolution Fourier transform infrared (FTIR) spectra acquired using a Perkin-Elmer 2000 FTIR spectrometer. Raman spectroscopy was performed using a Jobin–Yvon T64000 triple-stage spectrometer with a laser source at 325 nm and a spectral resolution of 2 cm⁻¹. Nitrogen adsorption–desorption isotherms measurements for all the synthetic samples were carried out by using an automatic microporous physical and chemical gas adsorption analyzer (ASAP 2020). The samples were outgassed at 150 °C for 2 h prior to the isotherm measurements. The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method. The average pore diameter and pore size distributions were evaluated using the Barrett-Joyner-Halenda (BJH) method by using the desorption branch of isotherms. The pore volumes were evaluated at a relative pressure (p/p0) of 0.99.

In H₂-TPR experiment, 10 mg samples were loaded in a quartz reactor, pretreated at 200 °C for 2 h under He gas flow, and cooled to 25 °C, following which the samples were heated to 700 °C with a 10 vol% H₂/Ar gas flow at a heat rate of 10 °C min⁻¹.

X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo ESCALAB 250 system (Thermo Fisher Scientific, USA) employed with AlK α radiation, operating at 150 W with the energy pass of 20 eV. The binding energies of various surface elements were calibrated using the C 1s peak at 284.8 eV.

Table S1 Data of the particle size calculated from the XRD patterns and TEM images and N_2 adsorption/desorption characterization for the MnBDC-300, MnBDC-400, and MnBDC-500 catalysts.

| Catalyst | $D_{XRD}^{a}(nm)$ | $D_{\text{TEM}}^{b}(nm)$ | $S_{BET}{}^{c}\left(m^{2}\!/g\right)$ | V_p^d (cm ³ /g) | $D_{p}^{c}(nm)$ |
|-----------|-------------------|--------------------------|---------------------------------------|------------------------------|-----------------|
| MnBDC-300 | 0.3 | 280 | 3 | 0.01 | 16.4 |
| MnBDC-400 | 8 | 155 | 45 | 0.15 | 13.6 |
| MnBDC-500 | 11 | 138 | 41 | 0.14 | 13.5 |

^a particle size calculated from the XRD patterns.

^b particle size calculated from the TEM images.

^c The BET specific surface area.

^d Total pore volume estimated at $p/p_0 = 0.99$.

^e pore diameter

| 2 | | | | | | |
|-----------|------------------|------------------|------------------|---------------|-------|----------------|
| Catalysts | Mn species (%) | | | O species (%) | | |
| | Mn ²⁺ | Mn ³⁺ | Mn ⁴⁺ | O_L | O_V | O _a |
| MnBDC-300 | 22.4 | 43.9 | 33.7 | _ | 12.0 | _ |
| MnBDC-400 | 21.5 | 45 | 33.5 | 60.4 | 27.5 | 12.1 |
| MnBDC-500 | 21.6 | 42.8 | 35.6 | 60.9 | 24.3 | 14.8 |

species over MnBDC-300, MnBDC-400, and MnBDC-500 catalysts obtained by XPS measurements.

Table S3 Comparison of the reported catalysts for the synthesis of EU from CO_2

and EDA in recent works.

| Cotolysta | Т | $P_{\rm CO2}$ | Time | Conv. | Sel. | Ref.[] | |
|---------------------------------------|------|---------------|-------|-------|------|-----------|--|
| Catalysis | (°C) | (MPa) | (min) | (%) | (%) | | |
| ZnO/KF/Al ₂ O ₃ | 180 | 1.0 | 240 | 96 | 89 | 45 | |
| Ce-BTC MOF | 160 | 0.5 | 720 | 21 | 98 | 46 | |
| CeO ₂ | 160 | 0.5 | 720 | 50 | 98 | 46 | |
| N-CeO ₂ | 160 | 0.5 | 720 | 64 | 99 | 46 | |
| M-CeO ₂ -573 | 160 | 0.5 | 720 | 95 | 99 | 46 | |
| MnO ₂ | 160 | 0.6 | 120 | 40 | 55 | 47 | |
| Mn_3O_4 | 160 | 0.6 | 120 | 12 | 37 | 47 | |
| Mn_2O_3 | 160 | 0.6 | 120 | 82 | 99 | 47 | |
| MnBDC-300 | 120 | 0.6 | 20 | 73 | 54 | This work | |
| MnBDC-400 | 120 | 0.6 | 20 | 96 | 99 | This work | |
| MnBDC-500 | 120 | 0.6 | 20 | 86 | 67 | This work | |