Supporting Information

Engineering Defects in Mn-Based Nanocatalysts via Atmosphere-Controlled Pyrolysis of Mn-BDC for Enhanced CO_2-to-Ethylene Urea Conversion

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Catalyst characterization

A D/MAX2500/PC powder diffractometer (Rigaku) with Cu Kα 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.

Scanning electron microscopy (SEM) images were obtained on a Gemini SEM 300 microscope (ZEISS).

Fourier transform infrared (FT-IR) spectra were tested in a Tensor 27 (Bruker) spectrometer based on the transmission mode with a resolution of 4 cm^{-1}. Each spectrum was based on 32 scans (4000–400 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.

X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo ESCALAB 250 system (Thermo Fisher Scientific, USA) employed with AlKα 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 .

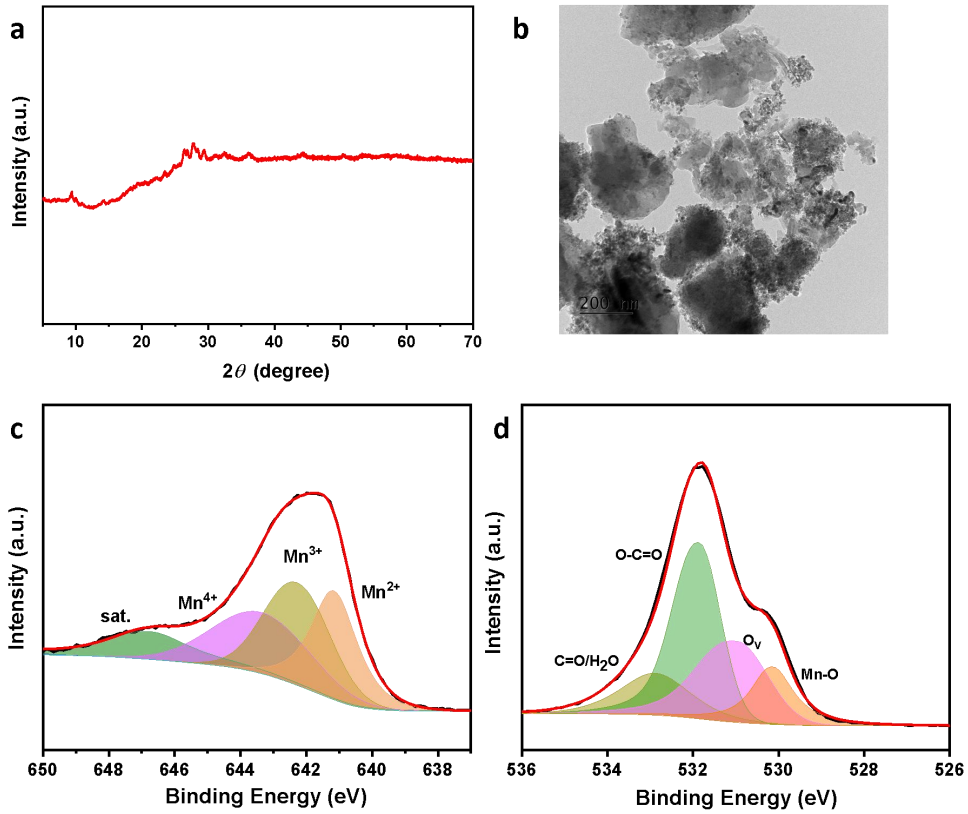

Fig. S1 XRD patterns, TEM images and Mn 3p and O1s XPS spectra of Mn-BDC-H-R4.

Table S1 Surface properties of the MnBDC-X samples.

Catalysts	S_{BET}[a] (m^2/g)	V_p[b] (cm^3/g)	D_p[c] (nm)	Mn^{3+}/Mn^{4+}	O_v (%)
MnBDC-A	45.5	0.15	15	1.51	28
MnBDC-H	8.4	0.043	21	2.44	39
MnBDC-N	9.4	0.046	20	1.75	32
MnBDC-H-R4	-	-	-	1.36	27

[a] The BET specific surface area.

[b] Total pore volume estimated at p/p_0 = 0.99.

[c] pore diameter

Table S2 Comparative catalytic activity data of MnBDC-X-400 catalyst with various reported catalysts for the synthesis of EU from CO_2 and EDA.

Catalysts	T (℃)	PCO_2 (MPa)	Time (min)	Conv. (%)	Sel. (%)	Ref.
CeO_2	160	0.5	720	50	98	
N-CeO_2	160	0.5	720	64	99	[42]
M-CeO_2-573	160	0.5	720	95	99	
MnO_2	160	0.6	120	40	55	
Mn_3O_4	160	0.6	120	12	37	[18]
Mn_2O_3	160	0.6	120	82	99	
MnBDC-300	120	0.6	20	73	54	
MnBDC-400	120	0.6	20	96	98	[24]
MnBDC-500	120	0.6	20	86	67	
MnBDC-A	100	0.6	10	77	81	
MnBDC-N	100	0.6	10	78	88	This study
MnBDC-H	100	0.6	10	93	95	