Supplementary Materials

Catalytic conversion of carbohydrates into 5-ethoxymethylfurfural by γ-AlOOH and CeO_2@B_2O_3 catalyst synergistic effect

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Materials and Methods

Catalyst characterization

The microstructures and morphologies of Boehmite (γ-AlOOH) and $CeO_2@B_2O_3$ was observed using a scanning electron microscopy (SEM) analysis (FEI Quanta PEG250). The crystalline structures and compositions were characterized by X-ray diffraction (XRD) with the X-ray powder diffractometer (Rigaku Ultimate IV), which using a Cu-Kα radiation source with a scanning range of 5° and 80° at a rate of 2° min^{-1}. X-ray photoelectron spectroscopy (XPS) was characterized by the Thermo Science ESCALAB 250XI system using a non-monochromatic Al-Kα radiation source. The N_2 adsorption–desorption isotherms were evaluated by Micromeritics ASAP2020 adsorption instrument at 77 K, and all the samples were degassed at 120 °C for 12 h under vacuum before the measurement. The specific surface area and the total pore volumes of the catalysts were evaluated in accordance with the methods of Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH), respectively. The stability of the catalyst was determined by Thermogravimetric analysis (TGA) using a TGA701 analyzer in the temperature range 30-500 °C with a heating rate of 10 °C min^{-1} under a N_2 atmosphere. The total acid density of catalysts was evaluated by the temperature-programmed desorption of ammonia (NH_3-TPD) method using a XianQuan TP-5080 chemisorption instrument. Prior to performing tests, 0.05 g sample was placed in a U-shaped quartz tube and purged at 300 °C with He of 99.9% purity for 2 h. After cooling to 120 °C, the sample was analyzed in a NH_3 atmosphere with a heating rate of 10 °C min^{-1} from 120 °C to 700 °C. The pyridine adsorption infrared spectroscopy (Py-IR) of the samples were recorded on the PerkinElmer Frontier infrared spectrometer. The solid acids were degassed at 300 °C in a vacuum (10^{-2} Pa) for 1 h. The saturated pyridine vapor was adsorbed at room temperature for 30 mins, and then desorbed by vacuum at 100 °C, 300 °C and 500 °C for 30 mins, respectively.

Quantification procedure for products

The EMF and HMF were determined by a UHPLC (Thermo Fisher U3000, America) instrument equipped with an ultraviolet detector (UV, 280 nm). The samples were separated by Aglient Eclipse XDB-C18 reversed-phase (200 mm × 4.6 mm), and the column temperature was kept an 30 °C. The mobile phase was acetonitrile and ultra-pure water with the volume ratio at 15:85, and the flow rate was 1.0 mL min^{-1}. Glucose and EG were quantified by a Shimadzu HPLC (Waters 2412)

with a refractive index detector, a Copsil NH_2 column (250 mm × 4.6 mm) was employed. A solution of deionized water and acetonitrile (3:7, v:v) at a flow rate of 1.0 mL min^{-1} was used as the mobile phase. The concentration of EL was detected by a DB-5 capillary column (50.0 m × 0.25 mm × 0.25 μm) in a GC (PerkinElmer Clarus 680, America) with a flame ionization detector (FID). The temperature procedure was as follows: the initial temperature of the column was 90 °C and stayed for 3 mins, then the temperature was increased to 210 °C with a heating rate of 10 °C min^{-1}, and was kept at 210 °C for 2 mins. During the process, the temperature of the injection and the FID detector were 250 °C and 280 °C, respectively. The nitrogen was used as carrier gas at a flow rate of 1.0 mL min^{-1}.

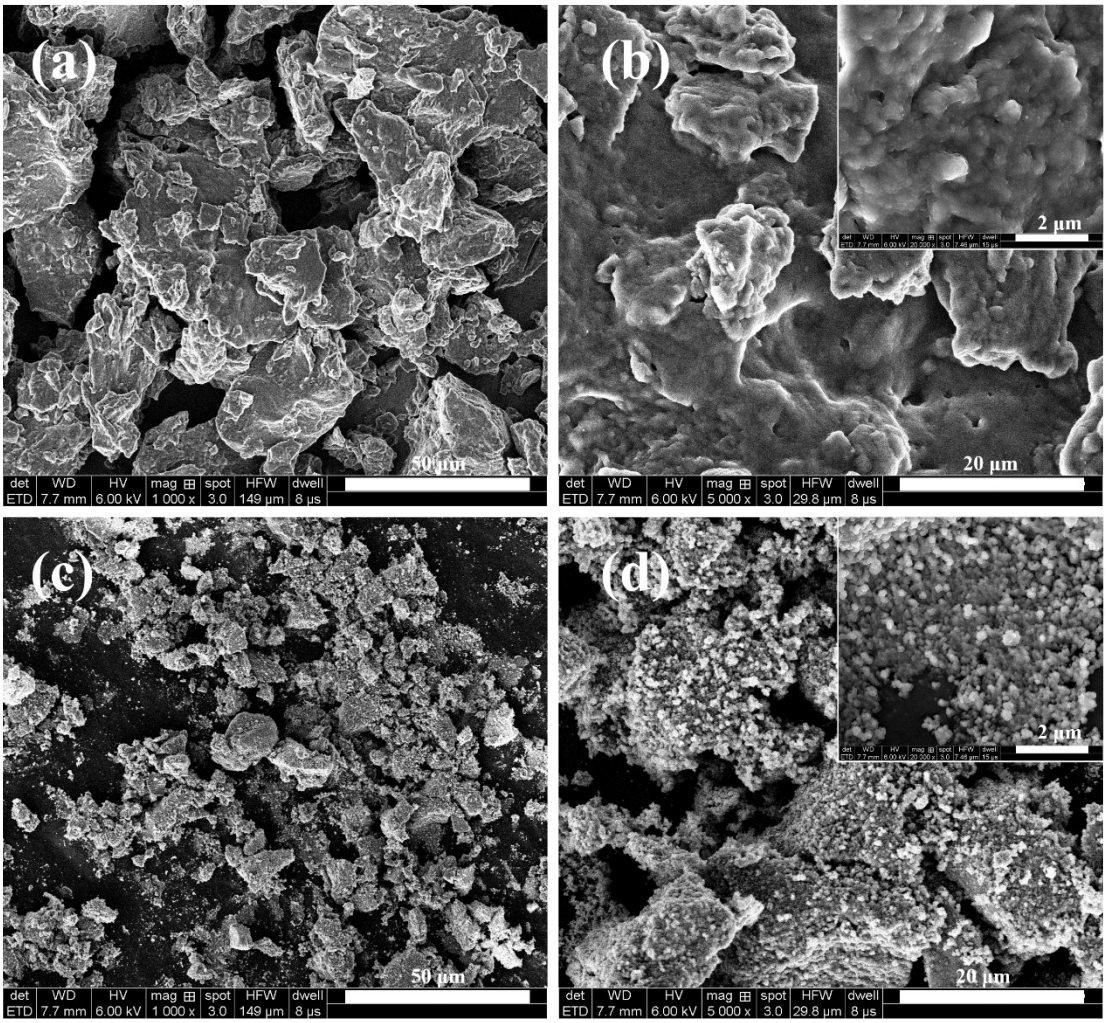

Fig. S1. SEM images of γ-AlOOH (a), (b) and CeO_2@B_2O_3 (c), (d).

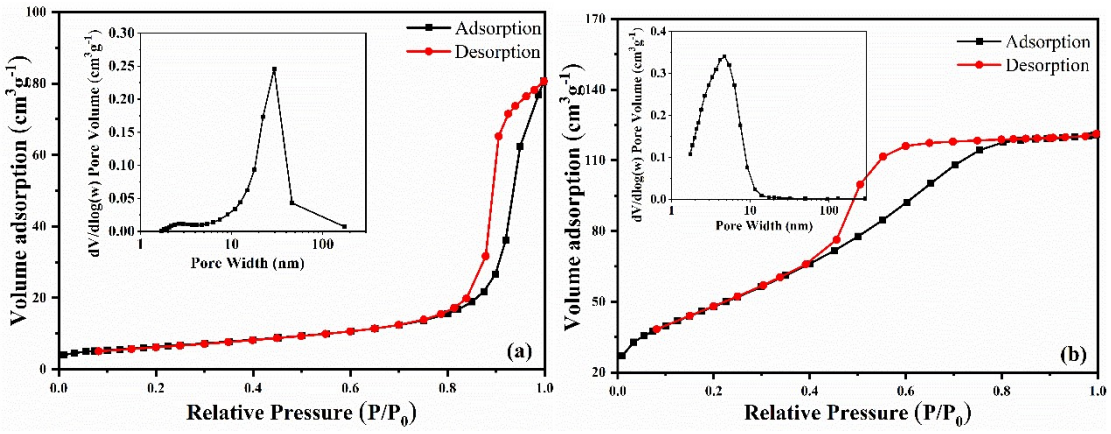

Fig. S2. N_2 adsorption/desorption isotherm and corresponding pore size distribution curve of CeO_2@B_2O_3/γ-AlOOH ((a): CeO_2@B_2O_3, (b): γ-AlOOH).

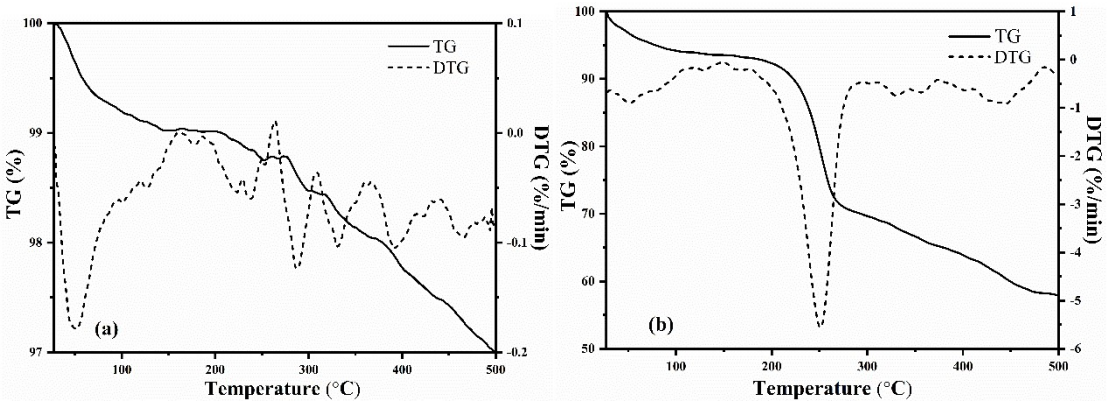

Fig. S3. Thermogravimetric (TG) curves of $CeO_2@B_2O_3$ (a) and γ-AlOOH (b).

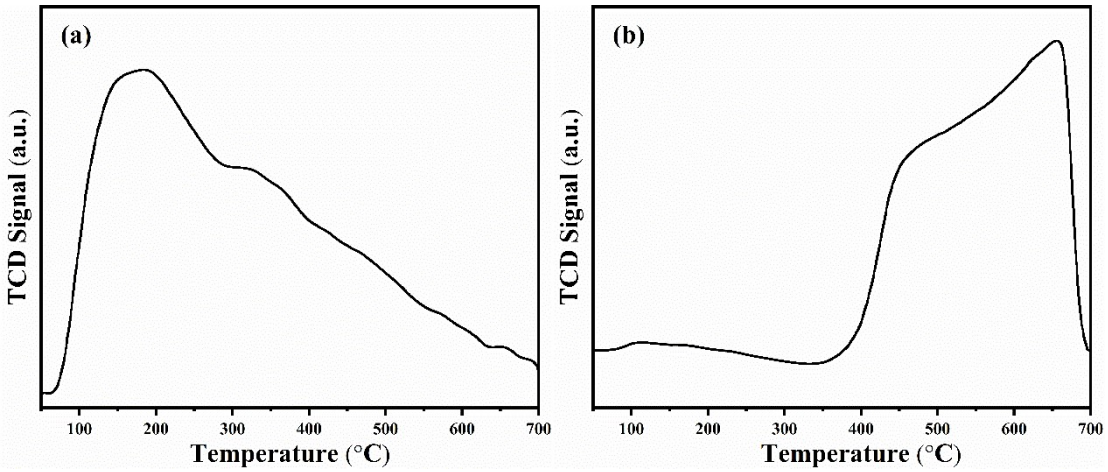

Fig. S4. NH_3-TPD curves of $CeO_2@B_2O_3$ (a) and γ-AlOOH (b).

Table S1. Specific surface area and pore parameters of $CeO_2@B_2O_3$/γ-AlOOH.

Catalyst	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
$CeO_2@B_2O_3$	22.4	0.1	22.2
γ-AlOOH	176.7	0.2	4.2

Table S2. Acidity distribution on catalyst surface at 100 °C, 300 °C, 500 °C.

Catalyst	Brønsted acidity (μmol/g)	Lewis acidity (μmol/g)	Brønsted acidity/Lewis acidity
$CeO_2@B_2O_3$ [a]	2.74	27.83	0.09
γ-AlOOH [a]	3.10	24.62	0.12
$CeO_2@B_2O_3$ [b]	1.23	11.62	0.10
γ-AlOOH [b]	0.99	12.68	0.07
$CeO_2@B_2O_3$ [c]	0.52	4.20	0.12
γ-AlOOH [c]	7.49	7.70	0.02

[a] Desorption temperature: 100 °C; [b] Desorption temperature: 300 °C; [c] Desorption temperature: 500 °C.

Table S3. Distribution of different acid sites with various catalyst ratios.

Entry	Catalyst		100 °C		300 °C		500 °C		Average		Brønsted acidity/Lewis acidity
	γ-AlOOH (mg)	CeO_2@B_2O_3 (mg)	Brønsted (μmol/g)	Lewis (μmol/g)	Brønsted (μmol/g)	Lewis (μmol/g)	Brønsted (μmol/g)	Lewis (μmol/g)	Brønsted (μmol/g)	Lewis (μmol/g)	
1	0	10	2.74	27.83	1.23	11.62	0.52	4.20	1.50	14.55	0.10
2	2	8	2.81	27.19	1.18	11.83	1.91	4.90	1.97	14.64	0.13
3	3	7	2.85	26.87	1.16	11.94	2.61	5.25	2.21	14.69	0.15
4	4	6	2.88	26.55	1.13	12.04	3.31	5.60	2.44	14.73	0.17
5	5	5	2.92	26.23	1.11	12.15	4.01	5.95	2.68	14.78	0.18
6	6	4	2.96	25.90	1.09	12.26	4.70	6.30	2.91	14.82	0.20
7	7	3	2.99	25.58	1.06	12.36	5.40	6.65	3.15	14.87	0.21
8	8	2	3.03	25.26	1.04	12.47	6.10	7.00	3.39	14.91	0.23
9	10	0	3.10	24.62	0.99	12.68	7.49	7.70	3.86	15.00	0.26

[a] The ratio of Brønsted acidity/Lewis acidity was averaged by the number of acid sites quantified at different temperatures for corresponding catalysts.

Table S4. Acidity distribution of catalysts with different catalyst loading ratios.

Entry	Catalyst		Weak acidity (mmol/g)	Medium-strong acidity (mmol/g)	Strong acidity (mmol/g)	Acidity ratio
	γ-AlOOH (mg)	CeO_2@B_2O_3 (mg)				
1	0	10	0.080	0.250	0.030	1.00:3.13:0.38
2	2	8	0.082	0.462	0.418	1.00:5.63: 5.10
3	3	7	0.083	0.568	0.612	1.00:6.84:7.37
4	4	6	0.084	0.674	0.806	1.00:8.02: 9.60
5	5	5	0.085	0.780	1.000	1.00:9.18:11.76
6	6	4	0.086	0.886	1.194	1.00:10.30:13.88
7	7	3	0.087	0.992	1.388	1.00:11.40:15.95
8	8	2	0.088	1.098	1.582	1.00:12.48:17.98
9	10	0	0.090	1.310	1.970	1.00:14.56:21.89