Electronic supplementary information (ESI)

Conversion of syngas into light olefins over the bifunctional ZnCeZrO/SAPO-34 catalysts: Regulation of the surface oxygen vacancy concentration and its relation to the catalytic performance

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As the Electronic supplementary information (ESI) of the manuscript “Conversion of syngas into light olefins over the bifunctional ZnCeZrO/SAPO-34 catalysts: Regulation of the surface oxygen vacancy concentration and its relation to the catalytic performance”, following materials are provided:

More characterization results for the Zn$_{0.5}$CeZrO$_x$ composite oxides prepared with different complexing agents and calcined at different temperatures; optimization of the reaction conditions for the conversion of syngas to olefins over the Zn$_{0.5}$CeZrO$_x$-glucose-500/SAPO-34 bifunctional catalyst.
Fig. S1. HR-TEM images of the Zn$_{0.5}$CeZrO$_x$ composite oxides prepared with different complexing agents: (a) Zn$_{0.5}$CeZrO$_x$-glucose, (b) Zn$_{0.5}$CeZrO$_x$-citric acid, (c) Zn$_{0.5}$CeZrO$_x$-tartaric acid, (d) Zn$_{0.5}$CeZrO$_x$-adipic acid, and (e) Zn$_{0.5}$CeZrO$_x$-L-alanine.
**Fig. S2.** TEM images and size distributions (estimated by counting more than 100 particles) of the Zn$_{0.5}$CeZrO$_x$ composite oxides prepared with different complexing agents: (a) Zn$_{0.5}$CeZrO$_x$-glucose, (b) Zn$_{0.5}$CeZrO$_x$-citric acid, (c) Zn$_{0.5}$CeZrO$_x$-tartaric acid, (d) Zn$_{0.5}$CeZrO$_x$-adipic acid, and (e) Zn$_{0.5}$CeZrO$_x$-L-alanine.

**Fig. S3.** N$_2$ adsorption-desorption isotherms (I) and corresponding pore size distribution curves (II) of the Zn$_{0.5}$CeZrO$_x$ composite oxides prepared with different complexing agents: (a) Zn$_{0.5}$CeZrO$_x$-glucose, (b) Zn$_{0.5}$CeZrO$_x$-citric acid, (c) Zn$_{0.5}$CeZrO$_x$-tartaric acid, (d) Zn$_{0.5}$CeZrO$_x$-adipic acid, and (e) Zn$_{0.5}$CeZrO$_x$-L-alanine.
**Fig. S4.** N\textsubscript{2} absorption-desorption isotherms (I) and corresponding pore size distribution curves (II) of the Zn\textsubscript{0.5}CeZrO\textsubscript{x}-glucose composite oxides (prepared with glucose as the complexing agent) calcined at different temperatures: (a) 400 °C; (b) 500 °C; (c) 600 °C; and (d) 700 °C.

**Fig. S5.** XRD patterns of the Zn\textsubscript{0.5}CeZrO\textsubscript{x}-glucose composite oxides (prepared with glucose as the complexing agent) calcined at different temperatures: (a) 400 °C; (b) 500 °C; (c) 600 °C; and (d) 700 °C.
Fig. S6. XRD patterns (I), N₂ adsorption-desorption isotherms (II) and corresponding pore size distribution curves (III) of the Zn₀.₅CeZrOₓ-glucose/SAPO-34 composite catalyst before (a, fresh) and after enduring the reaction of syngas to light olefins (b, spent).

Fig. S7. NH₃-TPD profiles of the SAPO-34 molecular sieve (a) and the Zn₀.₅CeZrOₓ-glucose/SAPO-34 composite catalyst (b).
Fig. S8. Raman spectra (I), O(1s) XPS spectra (II), and Ce(3d) XPS spectra (III) of the Zn$_{0.5}$CeZr$_x$O$_{4-x}$-glucose composite oxides (prepared with glucose as the complexing agent) calcined at different temperatures: (a) 400 °C; (b) 500 °C; (c) 600 °C; and (d) 700 °C.
Fig. S9. (I) CO-TPD profiles of the Zn$_{0.5}$CeZrO$_x$ composite oxides prepared with different complexing agents: (a) Zn$_{0.5}$CeZrO$_x$-glucose, (b) Zn$_{0.5}$CeZrO$_x$-citric acid, (c) Zn$_{0.5}$CeZrO$_x$-tartaric acid, (d) Zn$_{0.5}$CeZrO$_x$-adipic acid, and (e) Zn$_{0.5}$CeZrO$_x$-L-alanine. (II) Variation of the CO adsorption quantity obtained from CO-TPD with the concentration of surface oxygen vacancies of the Zn$_{0.5}$CeZrO$_x$ composite oxides measured by O 1s XPS. The desorption amount of CO was calculated according to the peak area between 150 and 350 °C in the CO-TPD profiles; as the desorption of CO on the ZnCeZrO composite oxide appears in general at 50–320 °C and levels off with the temperature above 350 °C, the recording of the CO-TPD profiles of several samples ends at 450–500 °C.

Fig. S10. CO conversion and products selectivity for the conversion of syngas over the Zn$_{0.5}$CeZrO$_x$-glucose/SAPO-34 bifunctional catalysts calcined at different temperatures (400, 500, 600 and 700 °C). Reaction conditions: H$_2$/CO = 2/1, 300 °C, 1.0 MPa, GHSV = 5400 mL/g·h, 30 h, Zn$_{0.5}$CeZrO$_x$/SAPO-34 = 1 (by mass); reported at a TOS of 30 h.
**Fig. S11.** Influences of the reaction pressure (I), gas hourly space velocity (II), and syngas H\textsubscript{2}/CO ratio (III) on the CO conversion and products distribution for the conversion of syngas over the Zn\textsubscript{0.5}CeZrO\textsubscript{x}-glucose-500/SAPO-34 bifunctional catalyst. Except that specified at the graph abscissa, the reaction was carried out under a H\textsubscript{2}/CO molar ratio of 2, 300 °C, 1.0 MPa, GHSV = 5400 mL g\textsuperscript{-1} h\textsuperscript{-1}, Zn\textsubscript{0.5}CeZrO\textsubscript{x}/SAPO-34 = 1 (by mass); the data were reported at a TOS of 15 h.