Supplementary Information for

Reaction intermediates recognized by *in-situ* FTIR spectroscopy in CO_2 hydrogenation over Cu/ZnO/SPP-zeolite catalyst

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S1: Synthesis and basic properties of the pure-silica SPP zeolite

SPP zeolite was synthesized according a procedure adapted from ref. [1]. A mixture of 24.9 g 25% aq. solution of tetra-n-butylammonium hydroxide and 16.67 g tetraethoxysilane was stirred in a sealed plastic bottle at room temperature for 24 hr., and at 115°C for another 48 hr. The solid product was recovered by high-speed centrifugation, washed with water, and freeze-dried. Calcination was performed at 550°C for 12 hours, with a heating ramp of 1°C/min.

XRD showed reflections in line with MFI framework, but broadened corresponding to the nanostructures (Figure S1a). SEM showed ellipsoidal particles of about 100 nm in length, consisting of intersecting nanoplates (Figure S1b). TEM showed that the thickness of the plates was about 2 nanometers (Figure S1c and S1d). There were voids between the intersecting nanoplates, providing space for encapsulation of guest particles. Figure S2 shows the N_2 adsorption/desorption isotherm at 79 K of the calcined

SPP zeolite and the associated analysis of the mesopore distributions. The t-plot evaluation showed a micropore volume of 0.075 cm^3/g, an external surface area of 474.5 m^2/g; the BJH analysis indicated a mesopore distribution between 2–8 nm.

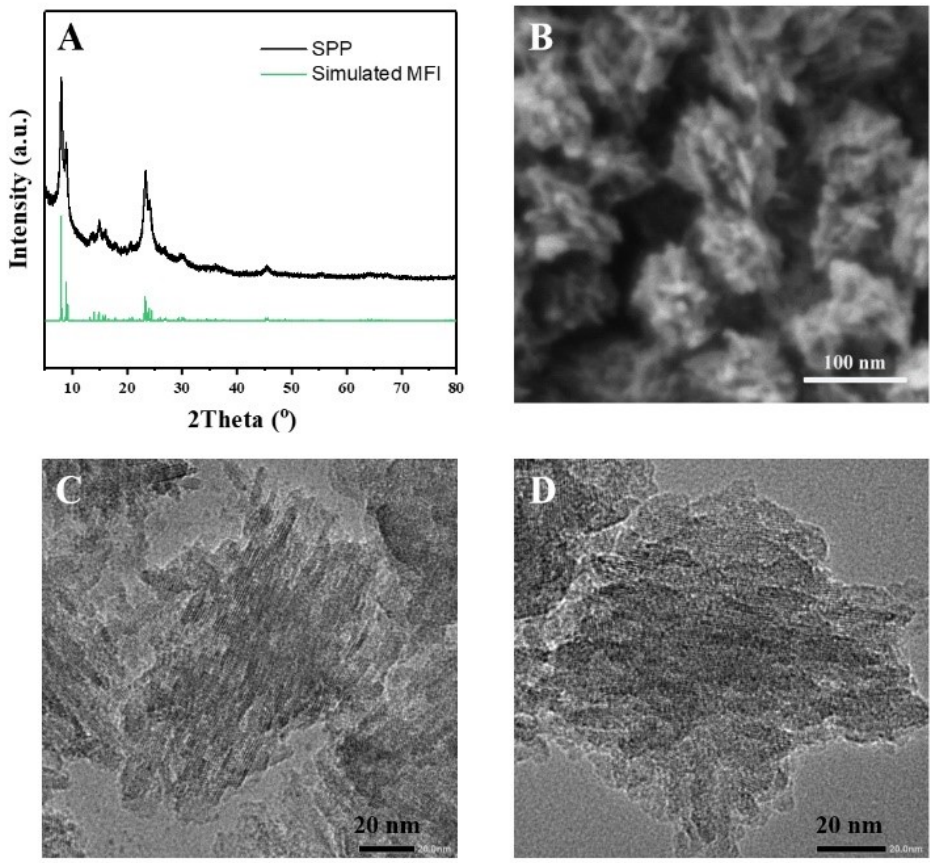

Figure S1. XRD pattern (A), SEM (B) and TEM (C and D) images of the SPP zeolite.

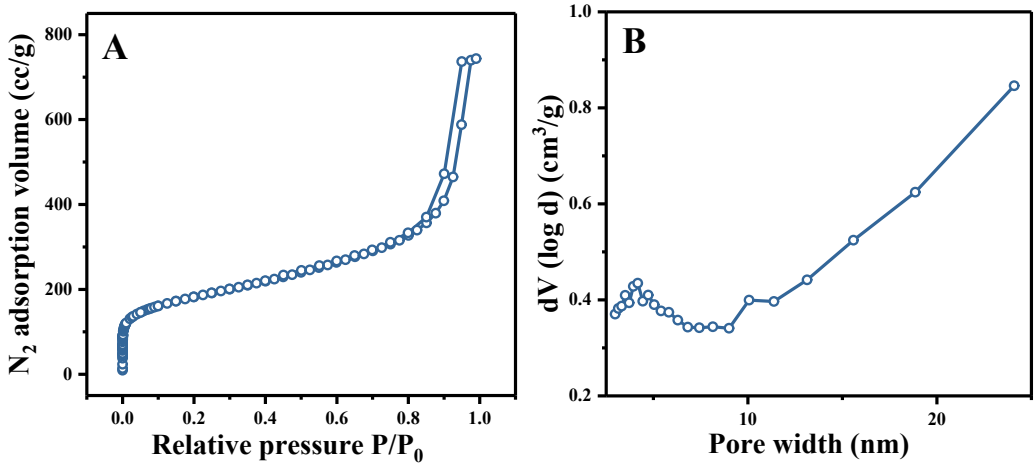

Figure S2. N_2 adsorption (A) and BJH pore-size distribution (B) of the SPP zeolite.

S2: *quasi-in-situ* XPS and *in-situ* FTIR studies

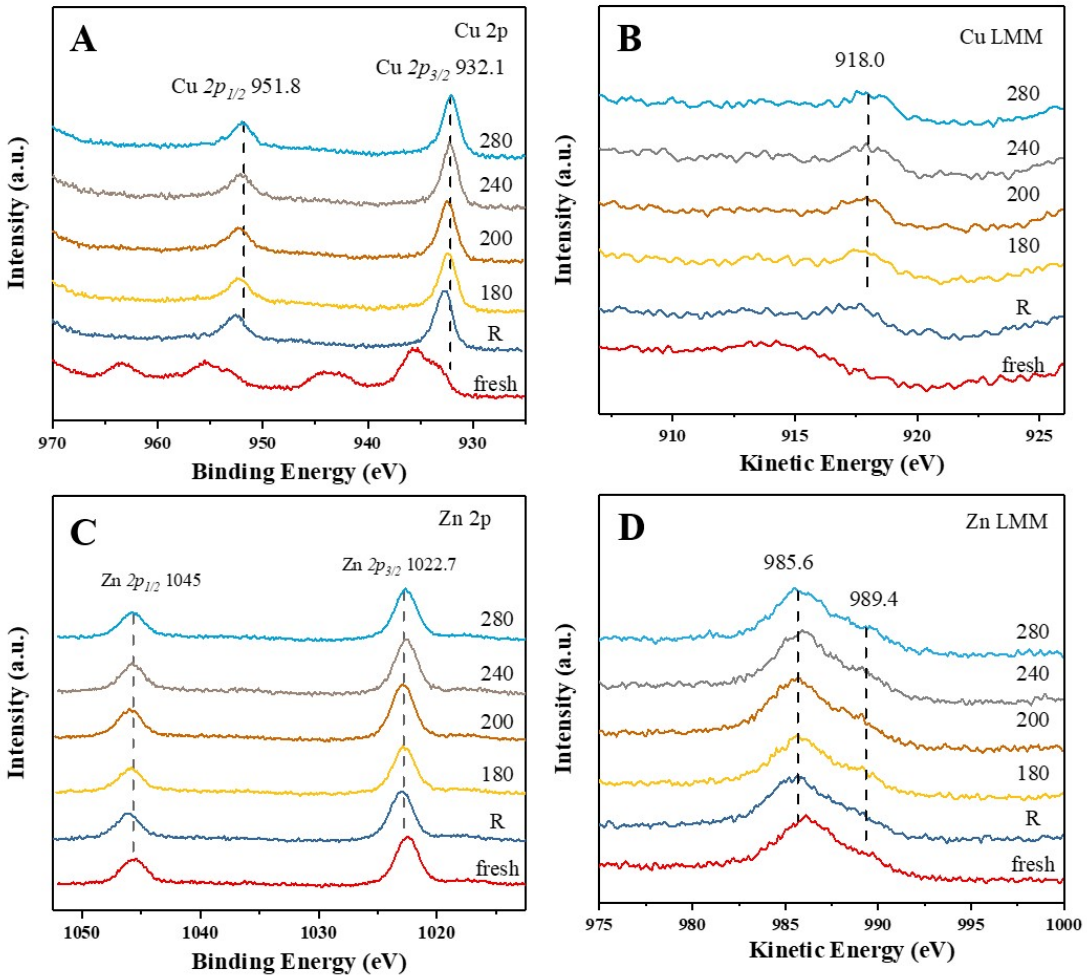

Figure S3. *quasi-in-situ* XPS spectra of CuZn-SPP : (A) Cu 2p, (B) Cu LMM, (C) Zn 2p, (D) Zn LMM.

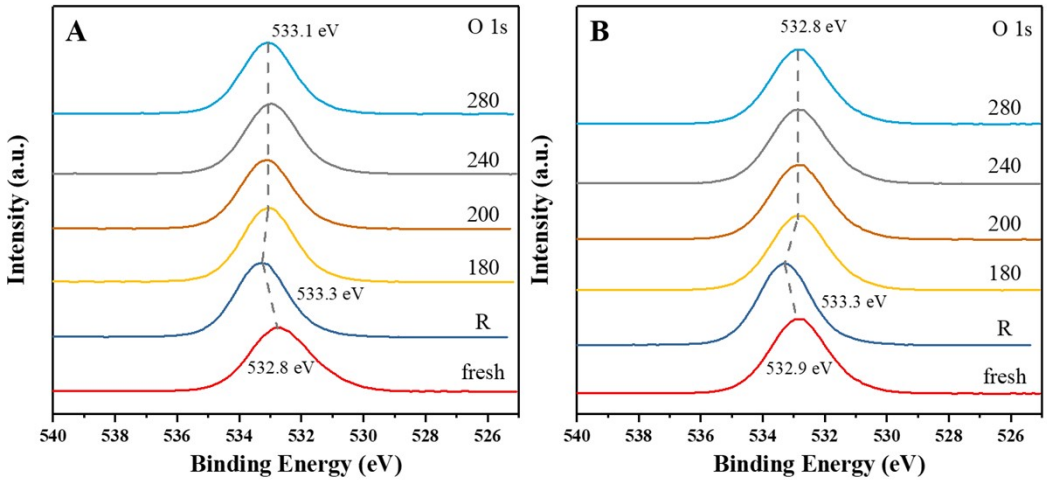

Figure S4. *Quasi-in-situ* O 1s XPS spectra of CuZn-SPP-E (A) and CuZn-SPP (B).

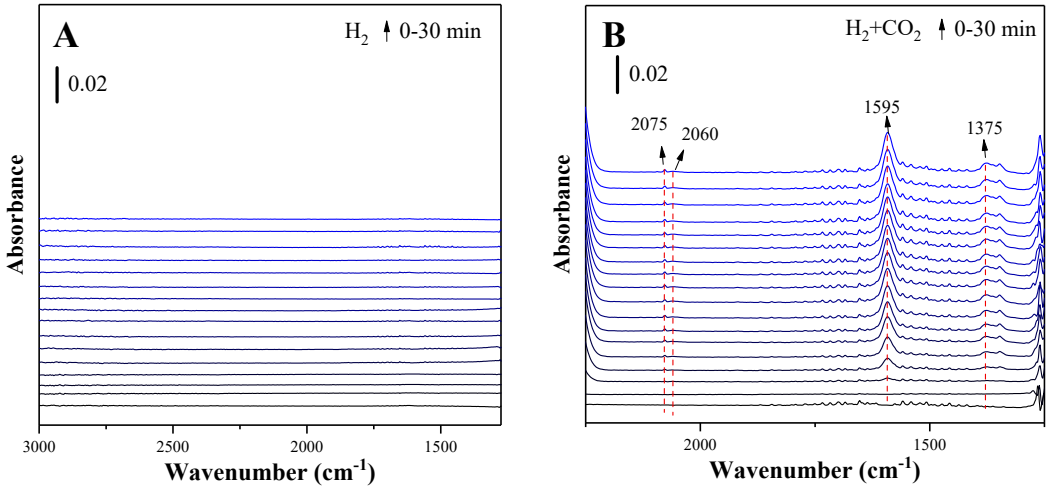

Figure S5. *in-situ* FTIR of CuZn-SPP-E in H_2 and then CO_2/3H_2 flow at 150°C.

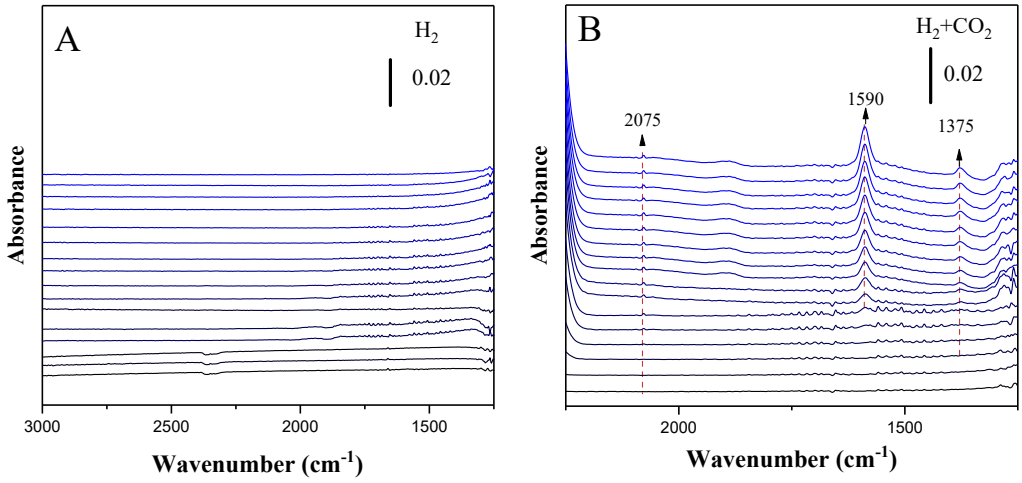

Figure S6. *in-situ* FTIR of CuZn-SPP H_2 and then in CO_2 /3H_2 flow at 150°C.

Reference

(1) Zhang, X.; Liu, D.; Xu, D.; Asahina, S.; Cychosz, K. A.; Agrawal, K. V.; Al Wahedi, Y.; Bhan, A.; Al Hashimi, S.; Terasaki, O.; et al. Synthesis of Self-Pillared Zeolite Nanosheets by Repetitive Branching. *Science* **2012**, *336* (6089), 1684-1687. DOI: 10.1126/science.1221111 (acccessed 2023/11/06).