Supplementary Materials for

The Lattice oxygen determines the methanol selectivity in CO_2 hydrogenation over $ZnZrO_x$ catalysts

This PDF file includes:

Table. S1. Catalytic performance of the $ZnZrO_x$ catalyst. Reaction conditions: 5.0 MPa, H_2/CO_2 = 3:1, GHSV = 24,000 mL/(g·h), 325 °C.

Catalyst	CO_2 Conversion (%)	Production Selectivity (%)			Yield	
		CH_3OH	CH_4	CO	(mg/(g_{cat}·h))	(mg/(m^2·h))
ZZ-200	3.59	45.18	0.35	54.21	137.9	4.4
ZZ-300	5.06	52.90	0.66	46.21	170.8	4.4
ZZ-320	5.18	72.17	0.2	27.48	273.4	5.9
ZZ-350	4.19	55.17	1.75	42.88	170.0	3.9
ZZ-400	4.08	41.42	4.83	53.53	126.2	4.5
ZZ-500	3.98	37.13	2.45	59.91	86.52	3.2
Zr/Zn=19	4.95	32.59	7.08	60.23	114.0	3.9
Zr/Zn=3	3.36	54.9	1.44	43.23	135.2	3.7
$ZnO-ZrO_2$	1.14	35.17	3.21	60.46	30.35	-

Table. S2. Catalytic performance of the $ZnZrO_x$ catalysts in literature for CO_2 hydrogenation to methanol.

Catalyst	Temperature (°C)	Pressure (MPa)	GHSV ($mL/g^{-1}·h^{-1}$)	H_2/CO_2	CO_2 Conversion (%)	CH_3OH Selectivity (%)
ZZ-320	325	5	24000	3	5.2	72.2
$ZnO-ZrO_2$(Zn/Zr = 1:1)[1]	320	3	24000	3	5.7	70.0
$Co_3O_4-ZrO_2$(Co/Zr =3:1)[1]	320	3	24000	3	1.9	1.0
$CuO-ZrO_2$(Cu/Zr = 3:1)[1]	320	3	24000	3	14.0	20.3
$ZnInO_x$[2]	300	2	24000	3	4.7	47.0
11.5%$GaZrO_x$[2]	300	2	24000	3	2.4	75.0
15ZnZr-600[3]	340	3	24000	3	7.4	55.8
$GaZnZrO_x$[4]	320	5	24000	3	8.8	85.0
ZrZn-15[5]	350	3	12000	3	7.0	50.0
20% $ZnO-ZrO_2$ (CP)[6]	320	5.5	24000	3	7.0	87.0
0.8%$PdZnZrO_x$[7]	280	5	24000	4	7.8	56.0
$ZnZrO_x$-RA[8]	320	5	24000		4.4	94.0
13$ZnZrO_x$,FSP[9]	320	5	24000	4	7.0	80.0
5.0% Zn-$CdZrO_x$[10]	320	5	24000	4	8.5	80.8
13%$ZnO-ZrO_2$[11]	320	5	24000	4	10.0	86.0

Table. S3. Arrhenius plots of CO_2 hydrogenation over ZZ-320 and ZZ-500.

Catalyst	Ea (KJ/mol)	Correlation factor
Z-200	24.45	0.97
ZZ-320	22.86	0.97
ZZ-500	35.64	0.99

Table. S4. Elemental content of ZZ-320 catalyst from EDS results

Element	Atomic (%)	Error（%）
O	47.07	0.30
Zn	9.41	0.26
Zr	43.52	0.08

Table. S5. d-spacings of catalysts calculated using the Bragg equation from XRD.

Catalyst	The average diameter of grains by XRD (nm)
ZZ-200	6.5
ZZ-300	7.2
ZZ-320	8.3
ZZ-350	7.4
ZZ-400	7.6
ZZ-500	6.3

Table. S6. The BET results from catalysts with various grinding speeds.

Catalyst	BET Surface Area(m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
ZZ-200	31.2	0.054	5.8
ZZ-300	38.5	0.0632	5.6
ZZ-320	46.5	0.0638	3.9
ZZ-350	43.3	0.0625	5.4
ZZ-400	28.1	0.0460	6.6
ZZ-500	27.1	0.0265	8.2

Table. S7. Deconvolution results of O 1s XPS peaks.

Catalyst	O species (%)		
	O_{I}	O_{II}	O_{III}
Zr/Zn=19	55.12	34.02	10.86
Zr/Zn=6	71.10	22.10	6.80
Zr/Zn=3	53.83	30.88	15.29

Table. S8. Quantitative results of the H_2-TPR, O_2-TPD, CO_2-TPD.

Catalyst	H_2 uptake in H_2-TPR (mmol/g)		CO_2 uptake in CO_2-TPD (mmol/g)		O_2 uptake in O_2-TPD (mmol/g)		
ZZ-320	**332°C**	**617°C**	**100 °C**	**408 °C**	**82 °C**	**461 °C**	**658 °C**
	0.0041	0.54	0.66	0.35	44.42	72.60	51.65
ZZ-500	**337°C**	**617°C**	**108 °C**	**414 °C**	**76 °C**	**444 °C**	**642 °C**
	0.0017	0.49	0.46	0.12	37.67	0.079	0.087

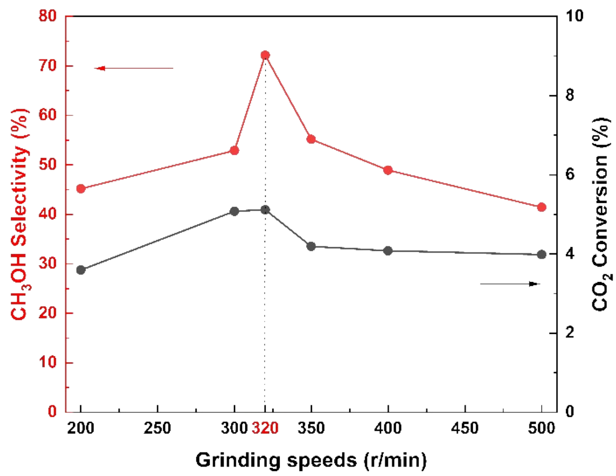

Fig. S1. The CO_2 conversion and the CH_3OH Selectivity of catalysts prepared with various grinding speeds. Reaction conditions: 325 °C, 5.0 MPa, H_2/CO_2 = 3:1, GHSV = 24,000 mL/(g·h).

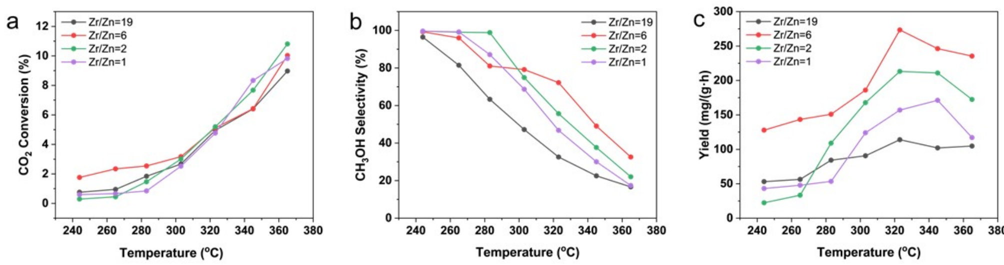

Fig. S2. Catalytic performance of the catalyst. (**a**) CO_2 conversion (**b**) CH_3OH selectivity and (**c**) CH_3OH yield of catalysts prepared at various Zr/Zn metal ratios. Reaction conditions: 5.0 MPa, H_2/CO_2 = 3:1, GHSV = 24,000 mL/(g·h).

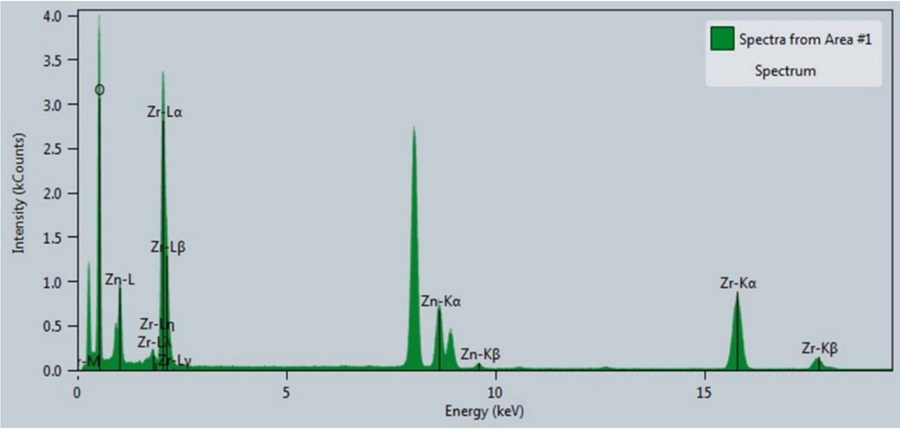

Fig. S3. The EDS element energy spectrum of ZZ-320 catalyst.

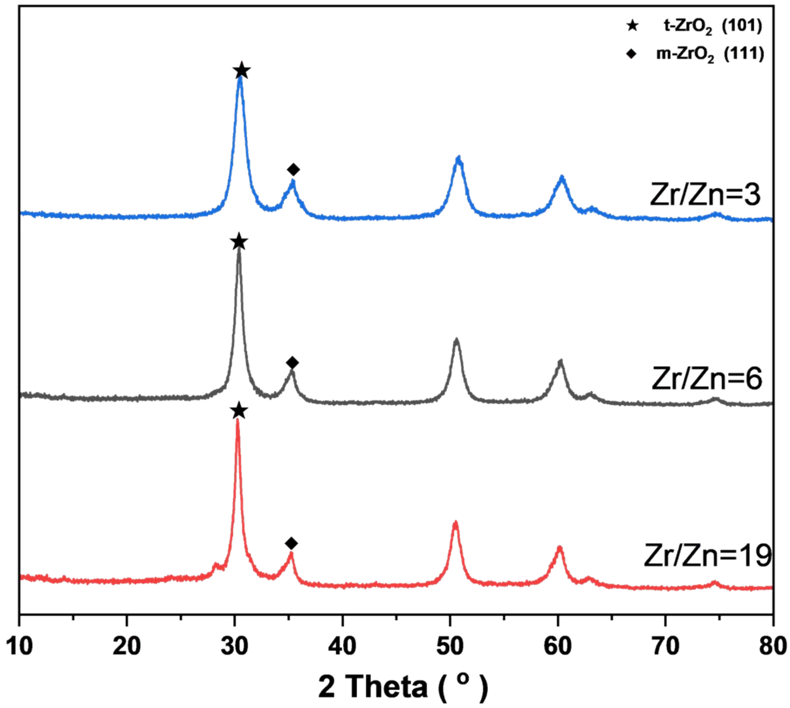

Fig. S4. XRD patterns of catalysts with different Zr/Zn ratios.

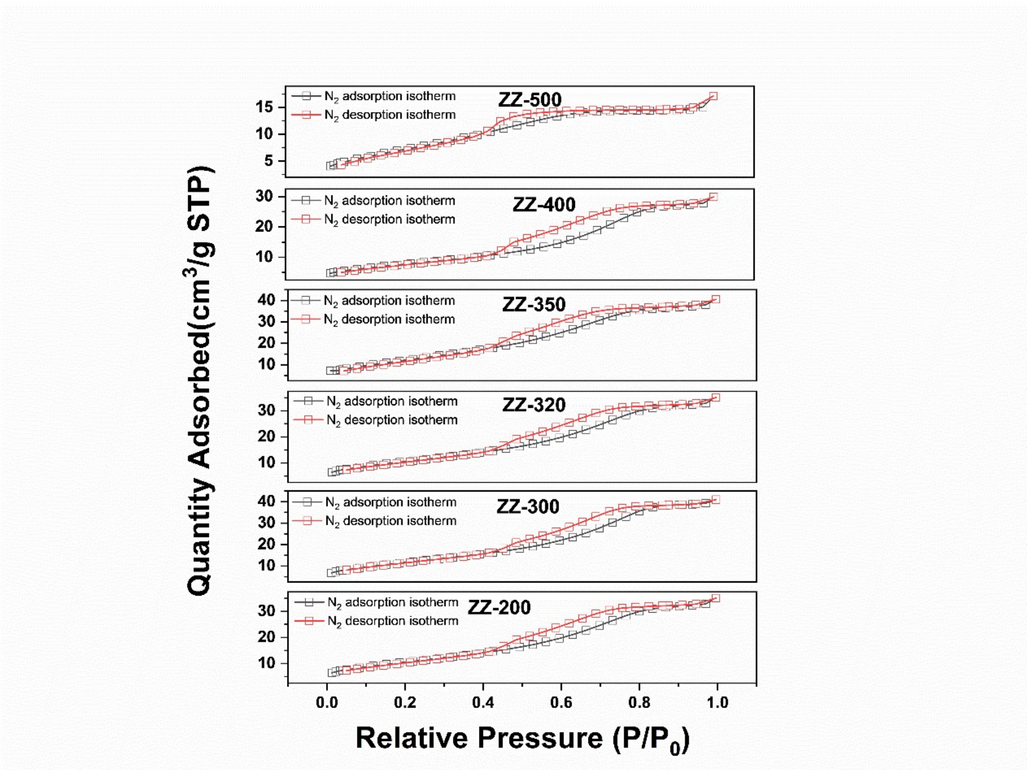

Fig. S5. Nitrogen adsorption-desorption isotherms of catalysts prepared with various grinding speeds.

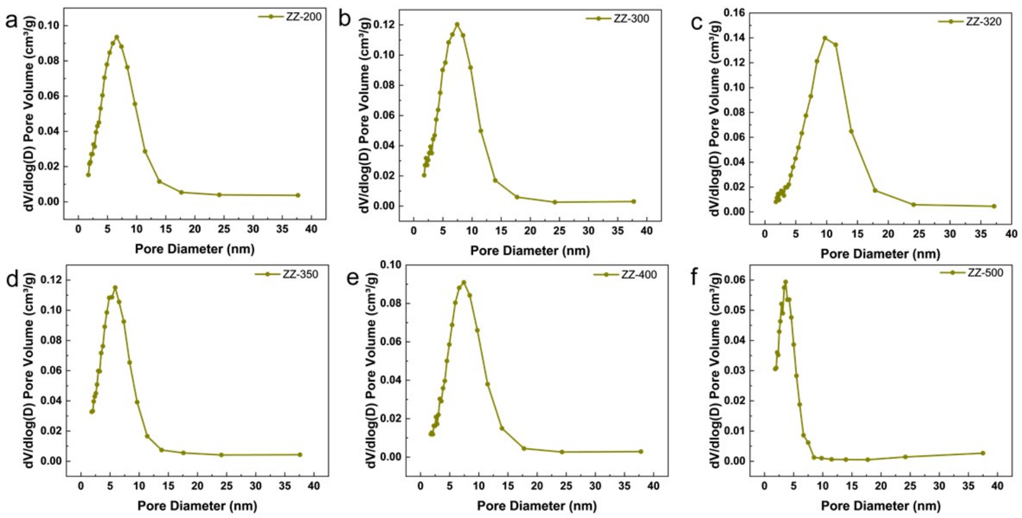

Fig. 6. Aperture distribution diagram catalysts prepared with various grinding speeds. (**a**)ZZ-200, (**b**)ZZ-300, (**c**)ZZ-320, (**d**)ZZ-350, (**e**)ZZ-400, (**f**)ZZ-500.

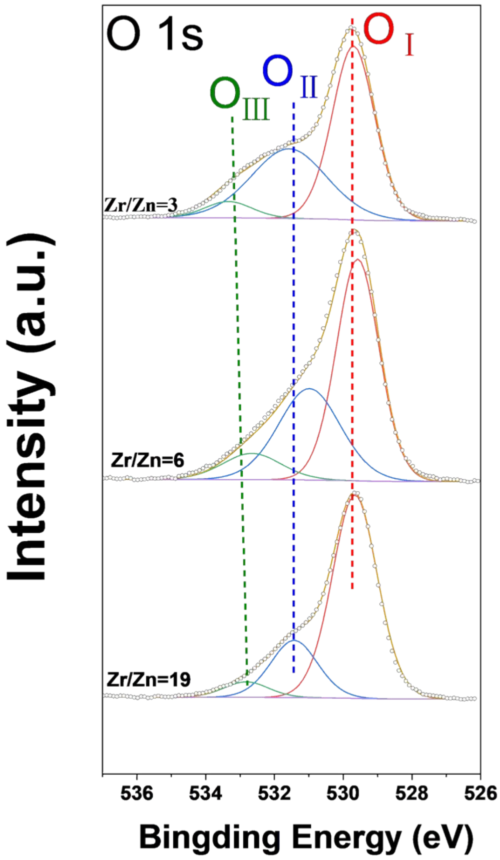

Fig. S7. O 1s XPS of catalysts with different Zr/Zn ratios.

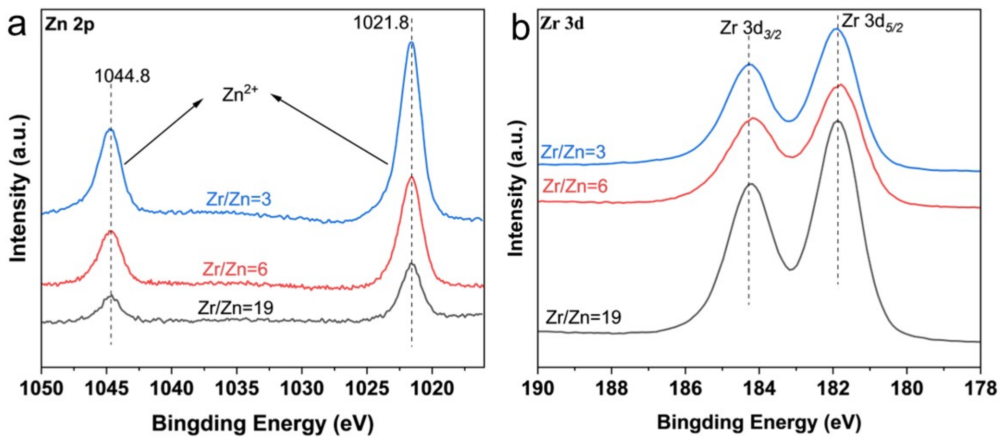

Fig. S8. Zn 2p (**a**) and Zr 3d (**b**) XPS of catalysts with different Zr/Zn ratios.

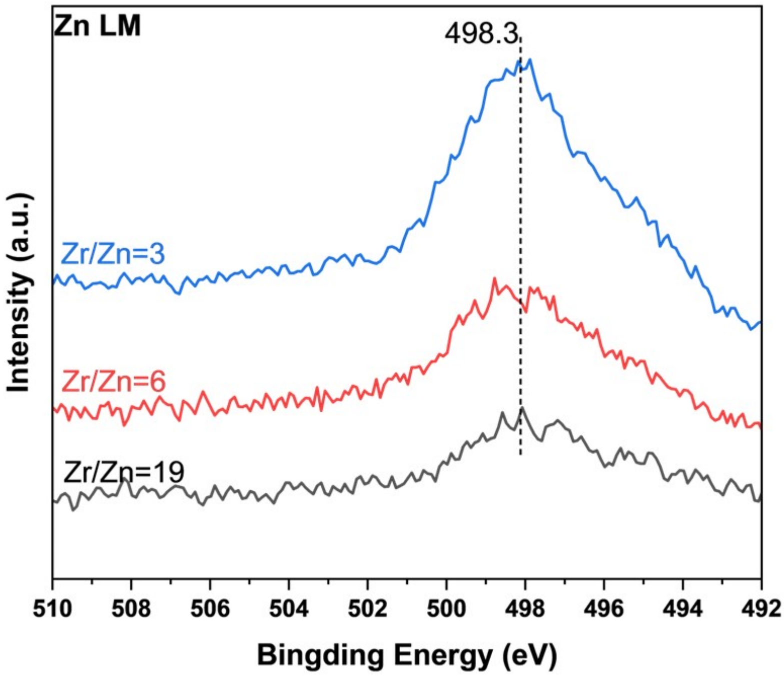

Fig. S9. Zn LM XPS of catalysts with different Zr/Zn ratios.

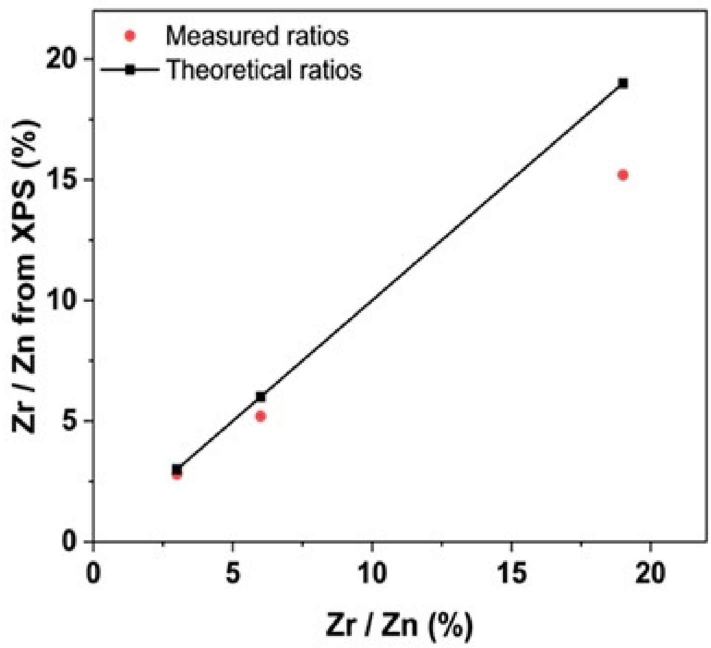

Fig. S10. Zr/Zn metal ratio in the surface region of ZnO-ZrO_2 measured by XPS.

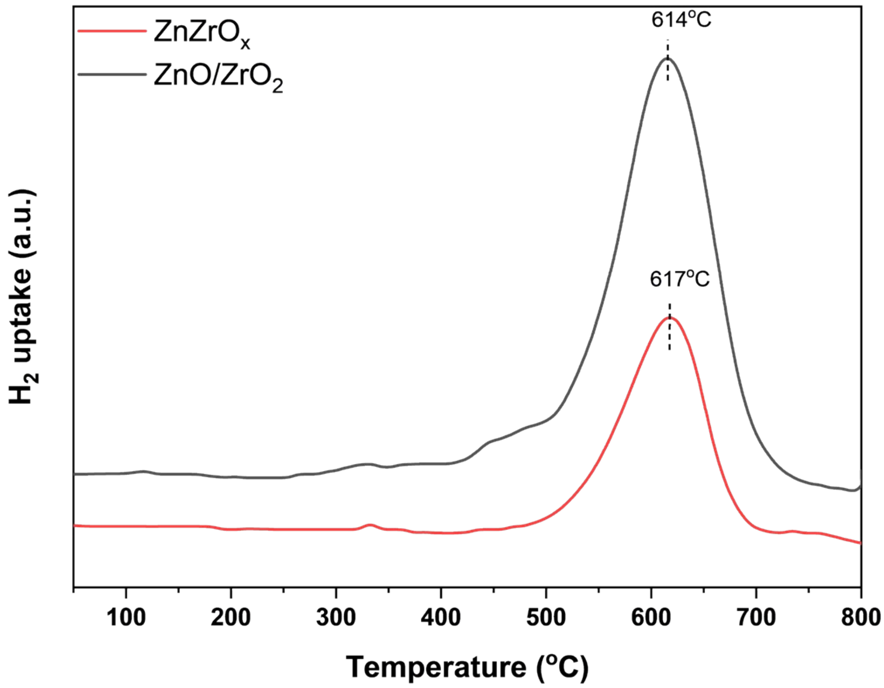

Fig. S11. H_2-TPR profiles of ZnO/ZrO_2 and $ZnZrO_x$ catalysts.

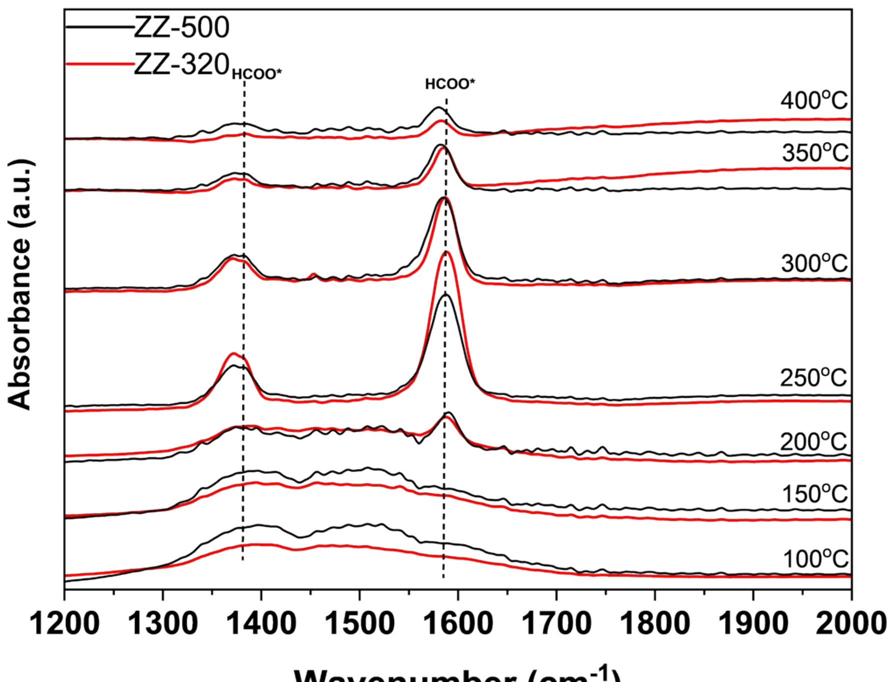

Fig. S12. Temperature-dependent in-situ DRIFTS spectra in H_2 over ZZ-320 and ZZ-500. (Conditions: 100–400 °C, 0.1 MPa, H_2, 40 mL/min, after reaction gas pretreatment).

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