Supplementary Information for:

A Mechanistic Study of Syngas to Light Olefins over OXZEO Bifunctional Catalysts: Insights into the Initial Carbon-Carbon Bond Formation on the Oxide

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1. Experimental details

1.1 Catalyst preparation.

ZnO, Ga_2O_3, and $ZnGa_2O_4$ were prepared by coprecipitation method similar to our previous reports.[1, 2] Three solutions of $Zn(NO_3)_3{\cdot}6H_2O$, $Ga(NO_3)_3{\cdot}xH_2O$ and mixed $Zn(NO_3)_3{\cdot}6H_2O$ and $Ga(NO_3)_3{\cdot}xH_2O$ (molar ratio = 1: 2) were prepared as salt precursors. An aqueous of sodium carbonate and sodium hydroxide was used as the precipitant. The temperature of the water bath was kept at 60 °C and the pH was maintained 9 ~ 10 during the whole process. The white precipitate was washed with deionized water and dried at 60 °C overnight, followed by calcination at 500 °C for 1 h in air.

H-mordenite (denoted as MOR) zeolites were purchased from Saint Chemical Materials.

1.2 Catalytic reaction tests.

Catalytic reactions were performed in a continuous flow, fixed-bed stainless steel reactor equipped with a quartz lining. The reaction was carried out under conditions of $CO{:}H_2$ = 1:2.5 (v/v)

at 673 K under 4.0 MPa. Typically, 300 mg of composite catalysts (20 ~ 40 mesh) with oxide: zeolite = 1:1 (m/m) was used.

Products were analyzed by an online GC (Agilent 7890B) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Ar of 5 % in concentration was included in syngas as the internal standard for online gas chromatography analysis. Hayesep Q and 5 Å molecular sieves packed columns were connected to the TCD, while HP-FFAP and HP-AL/S capillary columns were used with the FID. Oxygen-containing compounds and hydrocarbons were analyzed by FID, while CO, CO_2, CH_4, C_2H_4, and C_2H_6 were analyzed by TCD. CH_4, C_2H_4, and C_2H_6 signals were used as references to bridge the FID and TCD analysis. CO conversion was calculated on the carbon atom basis, i.e.:

$$conv_{\mathrm{CO}} = \frac{n_{\mathrm{CO,inlet}} - n_{\mathrm{CO,outlet}}}{n_{\mathrm{CO,inlet}}} \times 100\%$$

where $n_{\mathrm{CO,\ inlet}}$ and $n_{\mathrm{CO,\ outlet}}$ represent the moles of CO at the inlet and outlet, respectively. CO_2 selectivity ($sel_{\mathrm{CO_2}}$) was calculated according to

$$sel_{\mathrm{CO_2}} = \frac{n_{\mathrm{CO_2,outlet}}}{n_{\mathrm{CO,inlet}} - n_{\mathrm{CO,outlet}}} \times 100\%$$

Where $n_{\mathrm{CO_2,\ outlet}}$ denotes moles of CO_2 at the outlet.

The selectivity of individual hydrocarbon C_nH_m ($sel_{\mathrm{C_nH_m}}$) among hydrocarbons was obtained according to

$$sel_{\mathrm{C_nH_m}} = \frac{n_{\mathrm{C_nH_m,outlet}}}{\sum n_{\mathrm{C_nH_m,outlet}}} \times 100\%$$

1.3 Catalyst characterization.

X-ray diffraction (XRD) experiment was carried out on a PANalytical Empyrean-100 with a Cu Kα radiation source (λ = 1.5418 Å) and was operated at 40 mA and 40 kV. XRD patterns were recorded in the range of 2θ = 10 ~ 80°.

1.4 NMR experiments.

The *ex-situ* and *quasi-in-situ* studies of syngas conversion were carried out using premixed ^{13}C-syngas (^{13}CO:H_2 = 1:2.5) at 673 K under 4.0 MPa and 4 mL/ (min·150 mg_{cat}). After reacting for 7 minutes, 15 minutes, and 30 minutes, respectively, the reactor was quenched in liquid nitrogen. Then the samples were sealed into NMR rotors in glove box at room temperature.

The ^{13}C-isotopic labeling experiment was carried out using premixed syngas (CO:H_2 = 1:2.5) at 673 K under 2.0 MPa. After reacting for 5 min, the reactor was quenched in liquid nitrogen for NMR characterizations. For further reaction, ^{13}C-syngas was introduced into the pre-reacted catalyst, followed by a 10 min reaction at 673 K. Then the reactor was quenched in liquid nitrogen for the NMR characterizations. As a comparison, premixed syngas was introduced at 673 K and reacted for 15 min. Then the reactor was quenched in liquid nitrogen. All of the samples were sealed into NMR rotors in glove box at room temperature.

All the solid-state NMR experiments were carried out on a Bruker Avance Ⅲ 600 MHz spectrometer (14.1 T). For 1D ^{1}H-^{13}C cross-polarization experiments, the contact time of 1.5 ms

and 4 ms and spinning speed of 12 kHz were applied. And all the 2D ^{1}H-^{13}C HETCOR spectra were recorded with a contact time of 0.5 ms. J-based refocused ^{13}C-^{13}C INADEQUATE experiments were recorded with rotor synchronized delays about 2.5 ms and 3 ms. The chemical shift scale was calibrated using adamantane as external secondary reference.

1.5 Theoretical calculations.

Periodic DFT calculations were carried out with the projector-augmented-wave (PAW) method[3, 4] using the Vienna Ab Initio Simulation Package (VASP).[5-7] The generalized gradient approximation PBE functional[8] was employed to describe the exchange and correlation energies. An energy cutoff for the plane-wave-basis of 600 eV was applied for optimization of lattice parameter, while 400 eV for other calculations. The break condition for the electronic SC-loop was set to 1×10^{-5} eV, while for ionic relaxation loop it was 0.03 eV/Å. The Brillouin zone was sampled with 2×2×1 mesh of K-points for all surface species. Zero damping DFT-D3 method[9] was applied for van der Waals corrections. Improved dimer method[10] was used to search for transition state. The initial configuration was obtained by NEB method.[11, 12] Supercell of 2×2×1 was established based on (111) surface to make the interaction between absorbates negligible. A vacuum layer of 15 Å was added. For structure optimization, one third of the atoms at the bottom were kept fixed in bulk positions. Vibration calculation was also carried out with the surface species being relaxed and the oxide being fixed, in which ZPE and entropy corrections were taken into consideration at 673.15 K. Results show that there is only one imaginary frequency for transition state, indicating high reliability of this structure.

2. Supplementary Figures

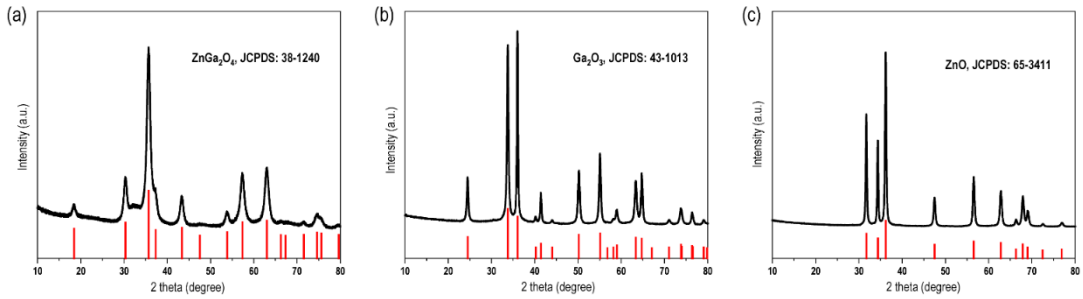

Fig. S1 XRD patterns of (a) $ZnGa_2O_4$, (b) Ga_2O_3, (c) ZnO.

$ZnGa_2O_4$, Ga_2O_3, and ZnO samples exist as spinel, α-Ga_2O_3, and wurtzite phases, respectively.

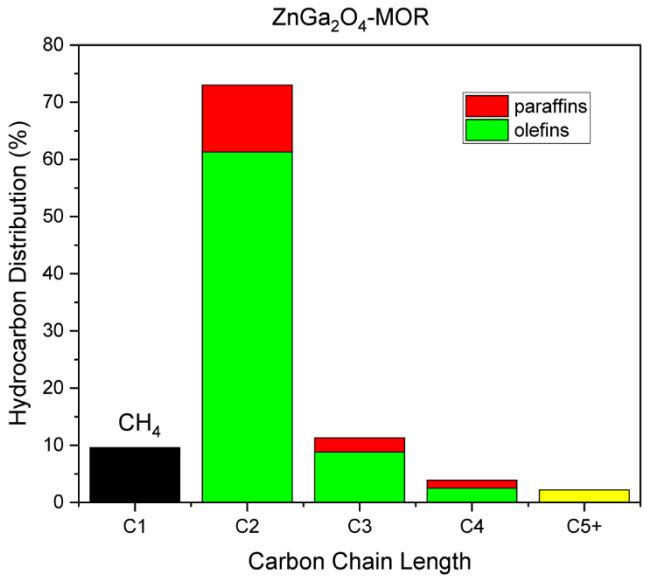

Fig. S2 Hydrocarbon distributions in syngas conversion over $ZnGa_2O_4$-MOR.

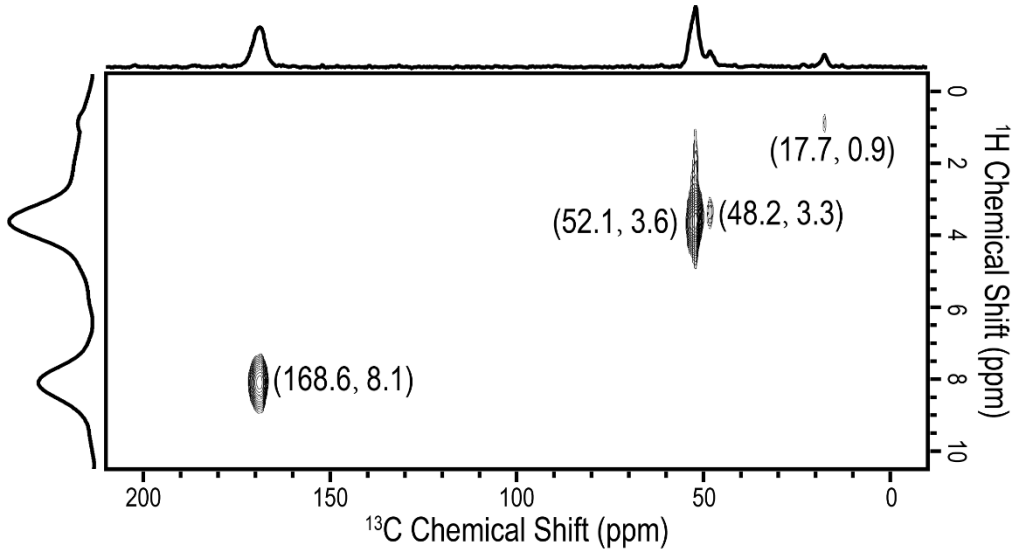

Fig. S3 2D ^{1}H-^{13}C HETCOR NMR spectra of surface species on ZnO after reacting with ^{13}C-syngas for 30 min at 673 K.

The species with ^{13}C signal at 168.6 ppm and ^{1}H at 8.1 ppm is consistent with the presence of formate species.[13] Two other correlations at ^{13}C (52.1 ppm)-^{1}H (3.6 ppm) and ^{13}C (48.2 ppm)-^{1}H (3.3 ppm), which corresponds to surface methoxyl and adsorbed methanol,[14] respectively. The species with correlation at ^{13}C (17.7 ppm)-^{1}H (0.9 ppm) is in the region of chemical shifts typical for methyl.[15]

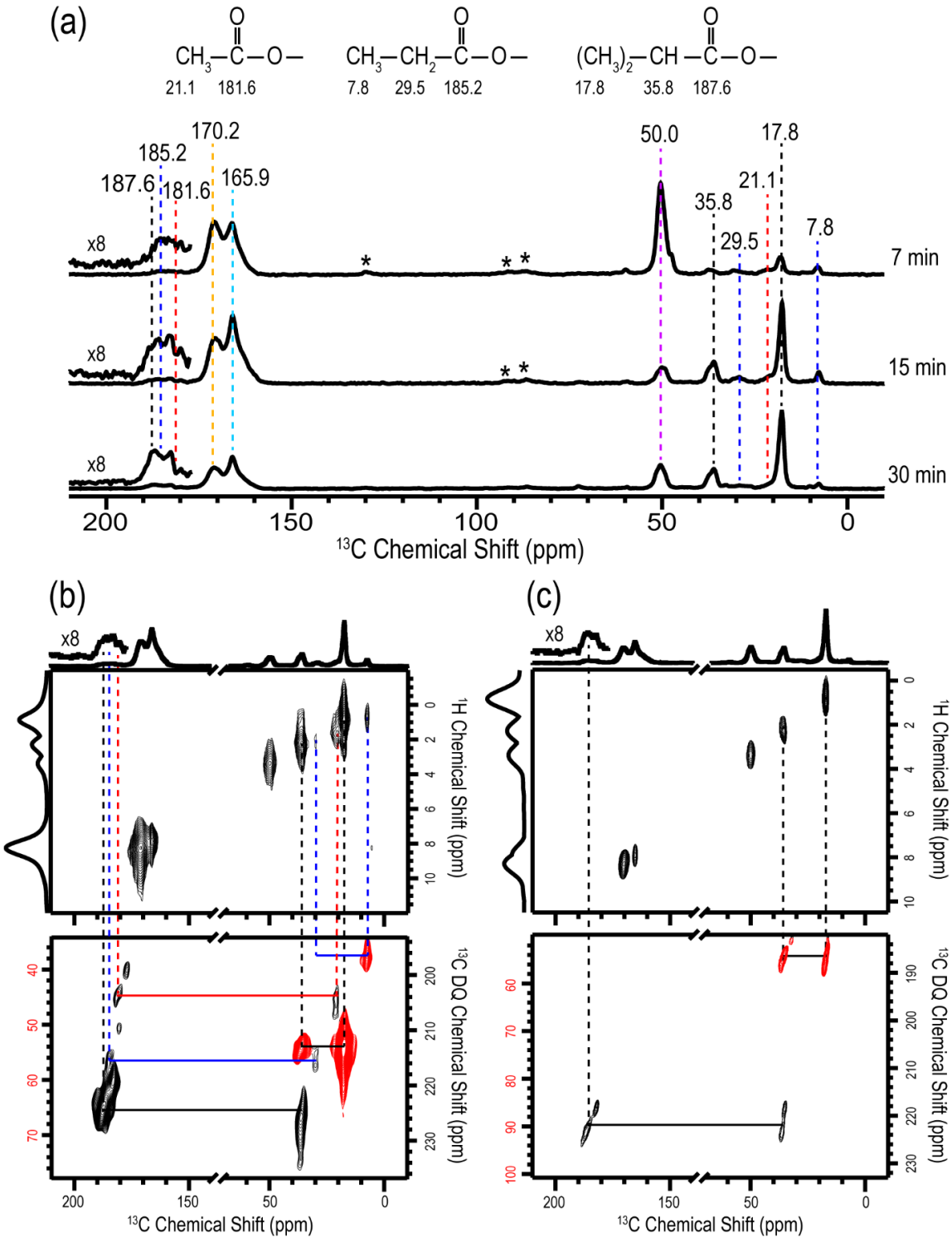

Fig. S4 (a) 1D ^{1}H-^{13}C CP/MAS NMR spectra of surface species on Ga_2O_3 after reacting with ^{13}C-syngas for 7 min, 15 min, and 30 min from top to bottom; (b) and (c) 2D ^{1}H-^{13}C HETCOR and 2D ^{13}C-^{13}C INADEQUATE NMR spectra of surface species on Ga_2O_3 after reacting with ^{13}C-syngas for 15 min and 30 min, respectively. Asterisk denotes spinning sidebands. The red correlation peaks denote the folded signals in the ^{13}C DQ dimension.

The ^{13}C signals at 170.2 ppm and 165.9 ppm, which are strongly correlated with ^{1}H resonances at 8.3 ppm and 7.9 ppm (HETCOR, upper spectrum of Figure S3b), respectively, are attributed to

two different types of formate.[16] The NMR signals of surface methoxyl shift upfield slightly (^{13}C/50.0 ppm and ^{1}H/3.4 ppm), comparing to $ZnGa_2O_4$. The J-based ^{13}C- ^{13}C correlations of ^{13}C (181.6 ppm)- ^{13}C (21.1 ppm), ^{13}C (185.2 ppm)- ^{13}C (29.5 ppm)- ^{13}C (7.8 ppm) and ^{13}C (187.6 ppm)- ^{13}C (35.8 ppm)-^{13}C (17.8 ppm) can be assigned to acetate,[17] propionate[18] and isobutyrate,[15, 19] respectively.

3. reference

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