## C–C Coupling Regulation to Enhance the Stability of Ambient Pressure Photothermal CO<sub>2</sub> Hydrogenation to Multi-Hydrocarbon Compounds

Xianhua Bai<sup>a</sup>, Linjia Han<sup>a,b</sup>, Jialin Wang<sup>c</sup>, Yanhong Luo<sup>a,b,d</sup>, Yiming Li<sup>a</sup>, Jiangjian Shi<sup>a</sup>, Yaguang Li<sup>\*c</sup>, Dongmei Li<sup>a,b,d</sup>, Qingbo Meng<sup>\*a,d,e</sup>

<sup>a.</sup> Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, P. R. China.

<sup>b.</sup> School of Physical Sciences, University of Chinese Academy of Sciences, Beijing, 100049, P.R. China.

<sup>c.</sup> Research Center for Solar Driven Carbon Neutrality, Engineering Research Center of Zerocarbon Energy Buildings and Measurement Techniques, Ministry of Education, The College of Physics Science and Technology, Institute of Life Science and Green Development, Hebei University, Baoding, 071002, P. R. China.

<sup>d.</sup> Songshan Lake Materials Laboratory, Dongguan, 523808, P. R. China

<sup>e.</sup> Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing, 100049, P. R. China.

\*Corresponding authors. Email: qbmeng@iphy.ac.cn; liyaguang@hbu.edu.cn.

## EXPERIMENTAL SECTION

**Chemicals:**  $Fe(NO_3)_3 \cdot 9H_2O$ ,  $Zn(NO_3)_2 \cdot 6H_2O$ , and  $KNO_3$  were purchased from Aladdin Co., Ltd. Polyvinylpyrrolidone (K30) was purchased from Macklin Co., Ltd, and while deionized water was generated in our laboratory.

The catalysts preparation: First, 4 g of PVP was dissolved in 20 ml of H<sub>2</sub>O. The resulting solution was subjected to stirring with a magnetic agitator while the following compounds were gradually incorporated: 0.0323 g of KNO<sub>3</sub>, 2.3799 g of  $Zn(NO_3)_2 \cdot 6H_2O$ , and 3.2318 g of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O. Following a stirring period of 30 minutes, the homogeneous solution was introduced dropwise into liquid nitrogen to facilitate rapid freezing. Subsequently, the frozen product underwent freeze-drying for a duration of 48 hours to eliminate water content. The dried product was subjected to calcination in a mixture of 10% H<sub>2</sub>/Ar at 600 °C for a period of 5 hours, employing a heating rate of 5 °C per minute. The final product was named Fe<sub>3</sub>C/ZnO. Following the same procedure as for Fe<sub>3</sub>C/ZnO, the Fe/NC sample was prepared without adding Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and KNO<sub>3</sub>.

**Characterizations:** XRD patterns was performed on a Bede D1 system operated at 20 kV and 30 mA with Cu K $\alpha$  radiation ( $\lambda$ = 1.5406 Å). Raman spectra were recorded on a HORIBA Raman spectrometer, with an excitation laser wavelength of 532 nm. The scanning electron microscopy (SEM) images were tested with the FEI Nova NanoSEM450 (Czech Republic). Transmission electron microscopy (TEM, ARM 200 F and JEOL F200+) was used to identify the morphology and the crystal structure of the nanostructures. Thermo ESCALAB-250 spectrometer with a monochromatic Al K $\alpha$  radiation source (1486.6 eV) was used to detect the valence state of materials. N<sub>2</sub>-sorption isotherms were collected on a Belsorb-Max system. <sup>57</sup>Fe Mössbauer spectroscopy was used at room temperature (298 K) in the transmission mode operating in constant

acceleration mode using a WISSEL WSS-10 spectrometer. A <sup>57</sup>Co in the Rh matrix was used as the Mössbauer source. The velocity drive transducer was operated in a triangular waveform mode over energy ranges of  $\pm 15$  mm/s. The spectrometer was calibrated using standard  $\alpha$ -Fe foil. The obtained spectra were quantitatively analyzed with the MossWinn program. In situ DRIFTS was recorded by a INVENIO S instrument (Bruker). In the reactor with H<sub>2</sub>:CO<sub>2</sub> = 3:1 (10 mL min<sup>-1</sup>of flow rate). All the spectra were recorded in the presence of CO<sub>2</sub>/H<sub>2</sub> mixtures in the gas phase, allowing complete saturation adsorption of the surface. Elements of Fe<sub>3</sub>C/ZnO was identified by Induced coupled plasma mass spectroscopy (ICP-MS) on a USA Thermo IRIS Intrepid II XSP ICP spectrometer.

**Photothermal CO<sub>2</sub> hydrogenation test:** A homemade light source that can be tuned from 0.1 to 2 kW m<sup>-2</sup> were used for photothermal test, and the uniform irradiation area of 0.8 m \* 0.3 m with 10 % light intensity fluctuation. Generally, 100 mg of prepared catalysts were loaded in TiC/Cubased photothermal device under ambient pressure. The reaction gas contained 72%H<sub>2</sub>, 24% CO<sub>2</sub> and 4% N<sub>2</sub> as an internal standard. The reaction products were detected by an online gas chromatograph (GC-7920), equipped with a 5A column connected to FID and a TDX-01 column connected to TCD for analyzing CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, CO and N<sub>2</sub>, and with a Plot Q column connected to FID for analyzing hydrocarbon products.

CO<sub>2</sub> conversion was calculated as follows:

$$CO_{2} \text{ conversion} = \frac{CO_{2 \text{ inlet}} - CO_{2 \text{ outlet}}}{CO_{2 \text{ inlet}}} \times 100\%$$
(1)

Where CO<sub>2 inlet</sub> and CO<sub>2 outlet</sub> are moles of CO<sub>2</sub> at the inlet and outlet, respectively.

CO selectivity was calculated according to:

$$S(CO) = \frac{CO_{outlet}}{CO_{2 inlet} - CO_{2 outlet}} \times 100\%$$
(2)

Where CO<sub>outlet</sub> refers to moles of CO at the outlet.

The selectivity for C<sub>2+</sub> (not include CO) was obtained according to :

$$S(C_{2+}) = \frac{\sum_{n=2}^{\max} nC_n H_{m \text{ outlet}}}{\sum_{n=1}^{\max} nC_n H_{m \text{ outlet}}} \times 100\%$$
(3)

Where  $C_nH_m$  represents moles of individual hydrocarbon product at the outlet, in which n refers to the carbon number.

The C<sub>2+</sub> production rate was calculated according to:

$$C_{2+} \text{ production rate} = \frac{CO_2 \text{ Conversion} \times (1 - S(CO)) \times S(C_{2+}) \times v(CO_2)}{24.5}$$
(4)

Where  $v(CO_2)$  refers to gas hourly space velocity of  $CO_2$  at the intlet.

**DFT calculation:** We have employed the Vienna Ab Initio Simulation Package (VASP) to perform all the spin-polarized density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the PBE formulation.<sup>1-3</sup> We have chosen the projected augmented wave (PAW) potentials to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 400 eV.<sup>4, 5</sup> Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller

than  $10^{-5}$  eV. A geometry optimization was considered convergent when the force change was smaller than 0.02 eV/Å. Grimme's DFT-D3 methodology was used to describe the dispersion interactions.<sup>6</sup>

The equilibrium lattice constant of BCC-Fe unit cell was optimized to be a=2.806 Å. We then use it to construct an Fe(110) surface model with  $p(4\times2)$  periodicity in the X and Y directions and 4 atomic layers in the Z direction separated by a vacuum layer in the depth of 15 Å to separate the surface slab from its periodic duplicates. Fe(110) model comprises of 64 Fe atoms. The equilibrium lattice constant of orthorhombic Fe<sub>3</sub>C unit cell were optimized to be a=4.401 Å, b=5.444 Å, c=6.811 Å. We then use it to construct an Fe<sub>3</sub>C(112) surface model with  $p(2\times1)$ periodicity in the X and Y directions and 2 stoichiometric layers in the Z direction separated by a vacuum layer in the depth of 15 Å to separate the surface slab from its periodic duplicates. This model comprises of 48 Fe and 16 C atoms. Zn<sub>6</sub>O<sub>6</sub>/Fe<sub>3</sub>C model was built by adding one Zn<sub>6</sub>O<sub>6</sub> cluster onto Fe<sub>3</sub>C model. During structural optimizations, a 2×2×1 k-point grid in the Brillouin zone was used for k-point sampling, and the bottom stoichiometric layer was fixed while the rest were allowed to relax.



Fig. S1 (a) C 1s, (b) N 1s, and (c) O 1s XPS spectra of Fe<sub>3</sub>C/ZnO catalyst.



Fig. S2 HRTEM image of  $Fe_3C/ZnO$ .



Fig. S3  $N_2$  adsorption-desorption isotherms of Fe $_3C/ZnO.$ 



Fig. S4 EDS element mapping of  $Fe_3C/ZnO$  catalyst for (a) Fe element, (b) Zn element. (c) overlay

of Fe and Zn elements.



Fig. S5 The picture for photothermal catalysis CO<sub>2</sub> hydrogenation.



Fig. S6 The  $CO_2$  conversion and hydrocarbon selectivity of Fe<sub>3</sub>C/ZnO catalyst under different light intensities.



Fig. S7 The XRD profiles of Fe/NC catalyst.

Fe/NC catalyst exhibited weak XRD peaks, which were assigned to Fe and FeO due to high carbon content.



Fig. S8 SEM images of Fe/NC.



Fig. S9 TEM image of Fe/NC.



Fig. S10  $N_2$  adsorption – desorption isotherms of Fe/NC.



Fig. S11  $CO_2$  conversion and CO selectivity of Fe/NC and Fe<sub>3</sub>C/ZnO.



Fig. S12 The  $CO_2$  conversion and hydrocarbon selectivity of Fe<sub>3</sub>C/ZnO catalyst at different space velocities.



Fig. S13 (a) The  $CO_2$  conversion and CO selectivity of Fe<sub>3</sub>C/ZnO catalyst during stability test. (b) The  $CO_2$  conversion and CO selectivity of Fe/NC catalyst during stability test.



Fig. S14 The structure model of Fe/NC.



**Fig. S15** TGA profiles of (**a**) Fresh Fe<sub>3</sub>C/ZnO and (**b**) test Fe<sub>3</sub>C/ZnO. TGA profiles of (**c**) Fresh Fe/NC and (**d**) test Fe/NC.



Fig. S16 SEM image of spent Fe<sub>3</sub>C/ZnO.



Fig. S17 XRD patterns of spent Fe<sub>3</sub>C/ZnO.



Fig. S18 Elemental mapping images of spent Fe<sub>3</sub>C/ZnO catalyst.

| K(wt%) | Fe(wt%) | Zn(wt%) |
|--------|---------|---------|
| 1.5    | 56.1    | 42.4    |

Table S1 Elemental analysis of  $Fe_3C/ZnO$ .

| Component         | IS (mm/s) | QS (mm/s) | B/T  | W (mm/s) | Area (%) |
|-------------------|-----------|-----------|------|----------|----------|
| Fe                | 0.27      | 0.94      | -    | 0.53     | 8.53     |
| Fe <sub>3</sub> C | 0.18      | 0.05      | 20.8 | 0.44     | 91.47    |

Table S2 Phase compositions of Fe $_3$ C/ZnO catalysts from mossbauer spectroscopy.

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