*Supporting Information*

# Promoter Effect on Carbon Nanosphere-Encapsulated Fe-Co Catalysts for Converting CO2 to Light Olefins

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## *Catalyst Evaluation*

The synthesized catalysts were tested using a standard procedure reported in a previously published work [46]. The testing procedure was carried out using a quartz tube (4 mm i.d., 6.35 mm o.d.) flow bed reactor at varying temperatures and ambient pressures. For each catalyst evaluation, approximately 0.1000 g of catalyst with a uniform mesh size of 40−60 was loaded into the quartz tube with two pieces of quartz wool to hold the catalyst in place. The catalyst was reduced in a 50% $H_2/N_2$ stream (40 mL min$^{-1}$ in total) at 350°C for 2 hours and then cooled down to 275 °C prior to $CO_2$ hydrogenation. The feed gas, $CO_2$, $H_2$, and $N_2$, with a 1/3/1 ratio (40 mL min$^{-1}$ in total), was introduced into the reactor at atmospheric pressure. The catalyst was then ramped from 275 °C to 400 °C at 25~50 °C increments. The product stream was analyzed online using a gas chromatographer (GC, Agilent 8890) equipped with a flame ionization detector (FID) and a thermal conductive detector (TCD). HP-PLOT Q capillary column was attached to FID for the separation and quantification of hydrocarbons. The Mol Sieve 5Å PLOT capillary column was attached to TCD for the detection of $N_2$, $H_2$, $CO_2$, CO, and $CH_4$. A sequence run was arranged in a queue to collect data at different temperatures. At each temperature, six GC data points were collected. The reaction parameters, such as $CO_2$ conversion (Eqn. 1), hydrocarbon distribution ($CH_4$, $C_2$-$C_4^=$, $C_2$-$C_4^0$, $C_{5+}$) (Eqn. 2), and selectivity (Eqn. 3), were defined as follows:

$$CO_2 \text{ Conversion} = \frac{n_{CO_2 \text{ (in)}} - n_{CO_2 \text{ (out)}}}{n_{CO_2 \text{ (in)}}} \times 100 \tag{1}$$

$$\text{Hydrocarbon distribution} = \frac{n_{\text{product i (out)}} \times \text{carbon number}}{\sum n_i \text{ (out)} \times \text{carbon number} - n_{CO} \text{(out)}} \times 100 \tag{2}$$

$$\text{Selectivity} = \frac{n_{\text{product(out)}} \times \text{carbon number}}{\sum n_i \text{ (out)} \times \text{carbon number}} \times 100 \tag{3}$$

where $n_{CO_2}$(in) and $n_{CO_2}$(out) are the number of moles of $CO_2$ fed and not converted, respectively. $n_{\text{product i}}$ refers to the mole of the product i; carbon number refers to the number of carbons contained in the product i; $\sum n_i$ (out) refers to the total number of moles of the carbon-containing products produced in the reaction.

*Metal analysis*

The contents of Fe and Co in the CNS was determined using ICP−MS (Agilent 7900 ICP−MS). The samples were first acid-extracted using concentrated $HNO_3$ (67−70%, VWR Aristar Plus for trace metal analysis) under intermittent sonication for 24 h, followed by filtration to remove carbon particles using a 0.45 μm syringe filter, and the clear filtrate was diluted to the estimated final concentrations in a range of 1−200 ppb using 1% $HNO_3$ aqueous solution. Eight standard solutions containing 0, 1, 5, 10, 30, 50, 100, and 200 ppb of Fe, Co, K, Na, Mn, Ce, Zn, respectively, were used to construct a standard calibration curve for calculating the specific metal concentration in sample solutions. ICP-grade $HNO_3$ (metal contents < 1 ppb) and HPLC-grade water (18.2 MΩ•cm, filtered by a 0.22 μm membrane filter) were used to prepare the sample and standard solutions.

*XRD-TGA-DSC-Raman measurements*

Powder XRD patterns were collected on a Bruker D8 Discover diffractometer using Cu Ka radiation (40 kV and 40 mA) with degrees per step and time/step parameters of 0.02° per step and 0.5 s/step, respectively, at a 2θ angle from 10 to 70°. XRD patterns were plotted in Origin and processed using the GSAS II software 34 to obtain structural information via Rietveld refinement. TGA was performed using a TA Q600 thermal analyzer. For a typical measurement, around 10 mg of catalysts were heated in an alumina pan from room temperature (~20 °C) to 650 °C at a 10 °C/min ramp rate with a 100 mL/min dry nitrogen purging rate. Raman analysis was performed using a Thermo Fisher DRX3 Raman micro spectrometer. The laser excitation source was a diode laser (λex = 785 nm). Spectra were recorded using the following materials and conditions: a stainless steel substrate, 50Å~ objective, collected exposure time of 30 s for eight accumulations, laser power of 1.5 mW (in focus), and an aperture of 50 μm slit. Raman spectra were recorded from ~five different sample spots depending on the homogeneity of the sample.