

Rationally Designed CuFe_2O_4 - Mesoporous Al_2O_3 Composite Towards Stable Performance of High Temperature Water-Gas Shift Reaction

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Electronic Supplementary Information (ESI)

Experimental

In the present study, poly (ethylene oxide) – poly (propylene oxide) –poly(ethylene oxide) block copolymers $[(\text{EO})_x(\text{PO})_x(\text{EO})_x]$ has been used as a soft template for the preparation of mesoporous material as reported earlier.¹⁻³ The Cu:Fe ratio of 1:2 was maintained in the total quantity of 10 mmol. In a typical synthesis, solution ‘A’ was prepared by adding 1g of $(\text{EO})_x(\text{PO})_x(\text{EO})_x$ in 10 ml of anhydrous ethanol. Similarly, solution ‘B’ was made with the combination of 10 ml of anhydrous ethanol, 1g $(\text{EO})_x(\text{PO})_x(\text{EO})_x$, corresponding nitrates of copper and iron and 1.6 ml of 67wt% HNO_3 . Both the solution A and B were allowed to stir separately for 4h. Meanwhile, a separate solution of 10 mmol of Al using aluminum iso-propoxide was prepared by using 10 ml of anhydrous ethanol and 1.6 ml of 67 wt% HNO_3 . Once dissolved it was added to solution A and then solution B was also mixed with solution A. To get a homogeneous mixture the entire mixture solution was kept for 5h of stirring. After that the gel formed was kept at 60 °C in oven for the solvent evaporation. The final catalyst CFO-MA was obtained after calcination at 400 °C for 5 h. CFO-MA was also calcined at 500 and 550 °C and characterized and evaluated for activity. The CFO catalyst (without alumina) was prepared by using only solution ‘B’, keeping remaining conditions such same.

Another set of catalyst with similar composition was prepared through impregnation method using Fe_2O_3 as a support. Based on the weight of the metal species said above the quantity of Fe_2O_3 , copper nitrate and aluminum nitrate were fixed. Initially, the corresponding weight of copper and aluminum nitrates were dissolved in minimum amount of water and allowed to stir. To that the support Fe_2O_3 was added slowly under stirring condition. After that the entire mixture was allowed to stir for 9 h and then kept at 100 °C in an oven for solvent evaporation. The final catalyst (I-CFO-A) was obtained after calcination at 400 °C for 5 h.

Characterization

BET surface area was measured by nitrogen adsorption at -196 °C using an ASAP 2010 (Micromeritics). Philips X'Pert Pro powder X-ray diffractometer using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) with a flat sample stage in the Bragg-Brentano geometry was used for XRD measurements. The diffractometer was equipped with a Ni filter and X'celerator as detector. Temperature programmed reduction (TPR) experiments were carried out in a BEL-CAT (BEL JAPAN INC.). Typically, 0.1 g sample was loaded into a quartz reactor. TPR was performed using 10% H₂ in Ar with a heating rate of 10 °C/min, from 20 to 1000 °C. The sensitivity of the detector was calibrated by reducing the known weight of NiO. A FEI TECNAI 3010 electron microscope operating at 300 kV (Cs = 0.6 mm, resolution 1.7 Å) was employed for high resolution transmission electron microscopy (HRTEM). Energy dispersive x-ray (EDX) analysis was carried out to measure the bulk composition of different materials. EDX measurements were performed on a SEM system equipped with EDX attachment (FEI, Model Quanta 200 3D). EDX spectra were recorded in the spot profile mode by focusing the electron beam onto specific regions of the sample.

Catalytic Reaction

Activity tests were carried out from 350 to 550 °C under atmospheric pressure in a fixed-bed micro-tubular quartz reactor with an inner diameter of 4 mm. The catalyst charge was 70 mg. T-union was employed at the exit of quartz reactor to install a thermocouple. A thermocouple was inserted into the catalyst bed to measure the reaction temperature. Unless otherwise mentioned, prior to each catalytic measurement, the catalyst was heated from room temperature to 400 °C at a heating rate of 4.6 °/min and then the temperature was maintained for 1 h. Afterwards, the temperature was decreased to 350 °C. The simulated reformed gas consisted of 17.02 vol% CO, 9.55 vol% CO₂, 1.03 vol% CH₄, 13.14 vol% H₂, 55.20 vol% H₂O, and 4.06 vol% N₂, which represents a typical syngas from waste gasifier that might enter the WGS reactor in a waste gasification system. The feed H₂O/(CH₄ + CO + CO₂) ratio was intentionally fixed at 2.0 to avoid coke formation.⁴ A GHSV value of 41,821 h⁻¹ was used to screen the catalysts in this study. Water was fed using a syringe pump and was vaporized at 150 °C upstream of the reactor. The product gas was chilled, passed through a trap to condense the residual water, and then analyzed on-line using an Agilent micro-gas chromatograph. To avoid any uncertainty the reaction was repeated at least three times with fresh catalysts and the results were quite reproducible within the error limit of $\pm 2\%$.

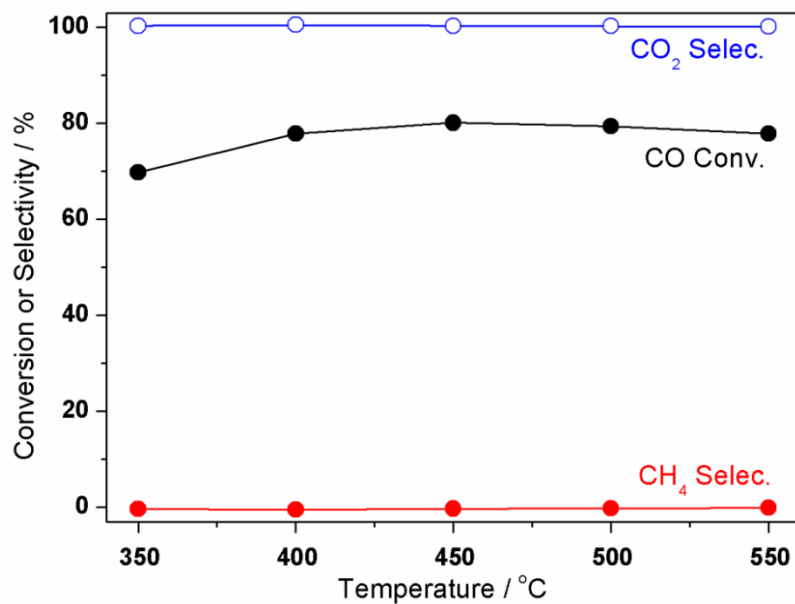


Fig. ESI-1: CO Conversion and CO₂ and CH₄ selectivity observed with CFO-MA nanocomposite at different temperatures. No methanation is an ultimate indication that no loss of hydrogen in the unwanted side reaction. This also indicates that the robust nature of porous alumina support, which acts as structural and textural promoter.

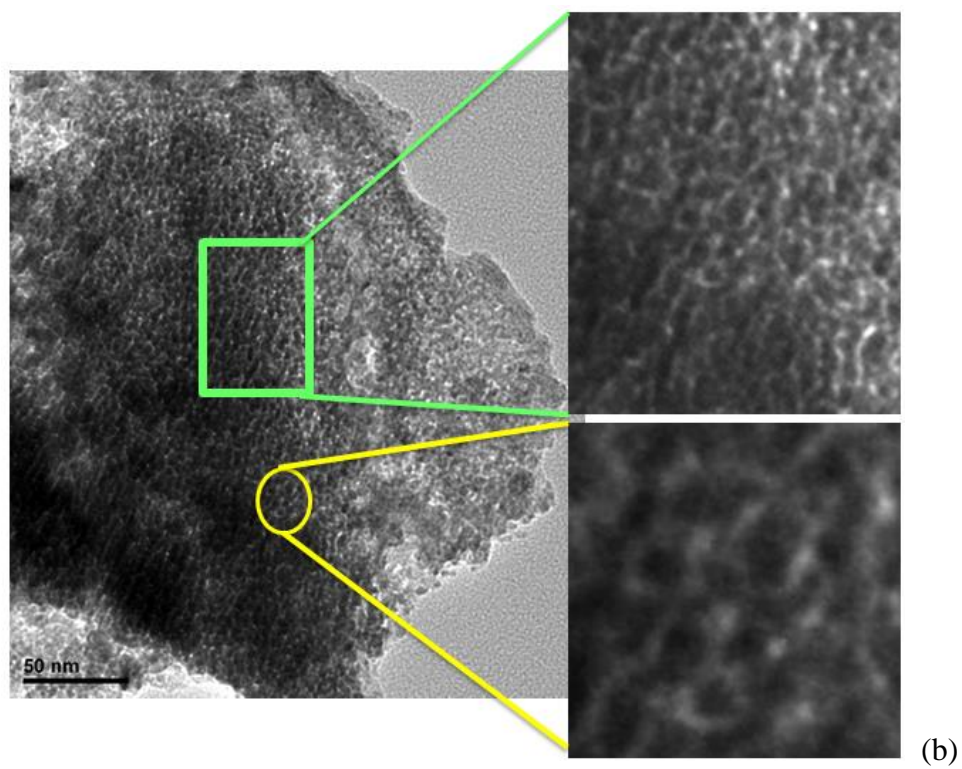
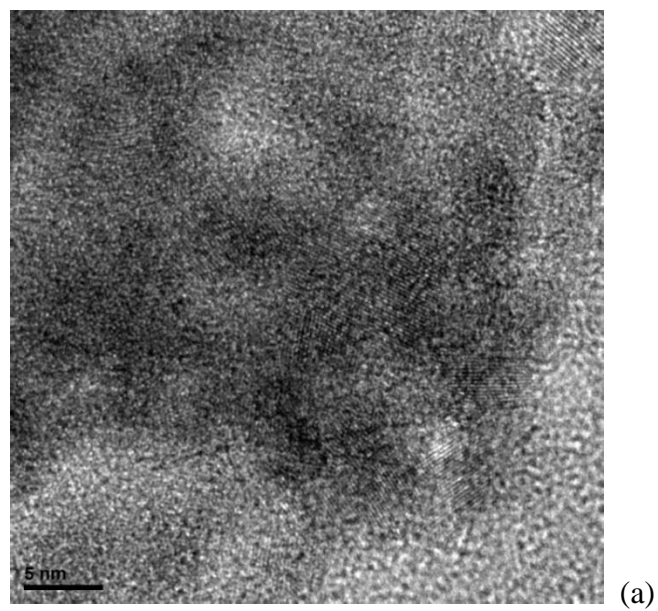


Fig.ESI-2: (a) Unaltered HRTEM image of CFO-MA. Except for the blue background in Fig. 2b (in main manuscript), both images are equivalent. (b) Near hexagonal mesopores are shown in the enlarged section.

ESI-3: Details of TPR Results

To get an insight into the nature of Cu promoter and the reduction pattern, all the catalysts were subjected to TPR experiment, and the results are shown in Figure 3a. Experimental traces are vertically shifted to avoid overlap. Commercial Fe-Cr shows a major reduction peak at 200 °C followed by an increasing reduction >350 °C. Peak at 200 °C is attributed to the reduction of CrO_3 to Cr_2O_3 .⁵ A shoulder below 200 °C is also observed on Fe-Cr catalyst is attributed to Cu-reduction. Indeed, EDX analysis supports the presence of Cu in the above commercial catalyst, which is generally added to increase the reducibility of Fe^{3+} to Fe^{2+} .⁶

Pure CuFe_2O_4 (CFO) shows a first reduction feature between 120 and 250 °C. This underscores a synergism between Cu and Fe species. However, this follows a second reduction >350 °C, like Fe-Cr. Interestingly, CFO-MA shows at least a shift in the first reduction peak by 40 °C to high temperature; first shoulder observed at 180 °C is attributed to highly dispersed Cu-species. This is followed by the typical CFO reduction peak at 250 °C. Second reduction peak begins at much higher temperatures (around 500 °C) with CFO-MA than other catalysts. Especially on CFO-MA, no reduction peak in the temperature region 400-450 °C, which corresponds to reduction of Fe^{3+} to Fe^{2+} , suggesting the existence of synergism between Cu promoter and Fe matrix.⁶ In contrast, I-CFO-A prepared through impregnation method showed various stages of transformation of Cu species. As reported earlier,⁷ there are four peaks observed, namely α_1 , α_2 , β , γ , occur at increasing temperature. The α_1 , α_2 is due to H_2 uptake of different oxygen environment. Whereas, β , γ peaks are due to the reduction behavior of Cu at the surface (highly dispersed state) and in the bulk. Additionally, the high temperature peak (424 °C) is attributed to the reduction of hematite to magnetite.⁶ This suggest, a lack of interaction between the Cu promoter and Fe matrix in I-CFO-A.

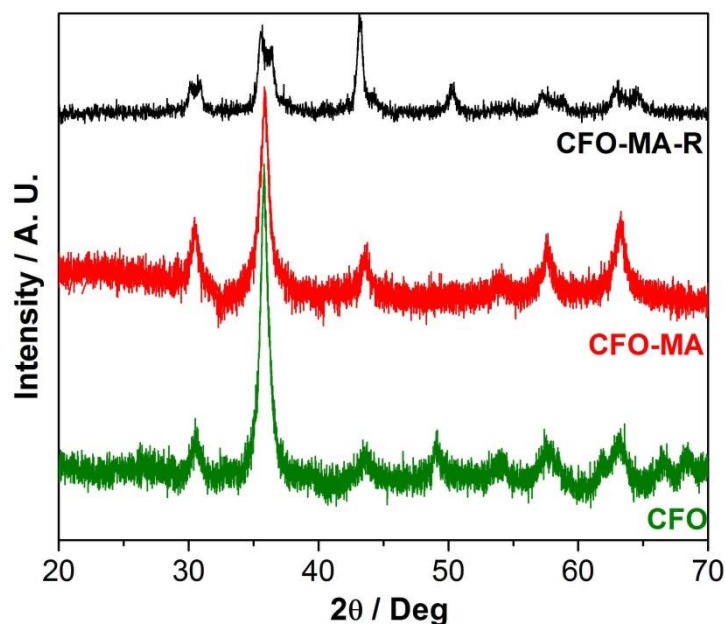


Fig.ESI-4: X-ray diffraction of pure CuFe_2O_4 (CFO) (JCPDS card no 34-0425) (green trace). In the used CFO-MA samples (black trace) the peak obtained at the 2θ value of 43.7 corresponds to metallic Cu (JCPDS card no 04-0836) overlaps with CuFe_2O_4 spinel feature at $2\theta = 43.2$. XRD of CFO-MA (red trace) is also given for confirmation and all major peaks from CuFe_2O_4 were observed in CFO-MA. A comparison of XRD features of CuFe_2O_4 and used CFO-MA (CFO-MA-R) confirms the presence of CuFe_2O_4 , after reaction. In addition to this the splitting of the peaks corresponding to CuFe_2O_4 (between $2\theta = 55$ and 65 deg) clarifies the presence of tetrahedral copper ferrite in used catalyst and indicates the structural integrity.

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