

Supplemental Materials

Carbon Nanotube Formation on Cr-Doped Ferrite Catalyst during Water Gas Shift Membrane Reaction: Mechanistic Implications and Extended Studies on Dry Gas Conversions

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Membrane fabrication

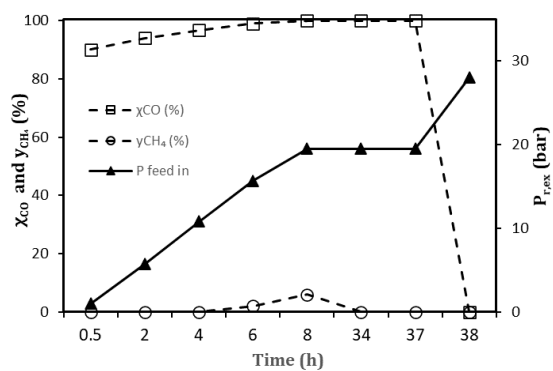
The tubular membrane support had a base wall, which had a porosity of ~30% and an average pore size of ~2 μm , and a ~25 μm -thick top-layer on outer surface, which had a porosity of ~30% and average pore size of ~50 nm. The 10-cm long tube had glaze coating seal over a 2.5-cm long section in each end that gave a 5-cm long active membrane section in the middle (i.e. active membrane area of 8.95 cm^2). The procedures for the zeolite membrane synthesis on the tubular support was detailed in our previous publication ^[1]. The H_2 -permselective membrane was fabricated by the in situ crystallization method and modified by the catalytic cracking deposition (CCD) technique. ^[2,3] The in-situ crystallization process used a clear synthesis solution with a molar composition of 0.055 SiO_2 (Aldrich): 0.0058 NaOH (Aldrich): 0.017 tetrapropylammonium hydroxide (TPAOH, Aldrich): 0.923 H_2O . The TPAOH was used as the structure directing agent (SDA) for the MFI zeolite. The zeolite membrane layer was formed by hydrothermal treatment in a horizontally placed and rotated autoclave at 180 $^\circ\text{C}$ for 6 – 8 h. The resultant MFI zeolite membrane tube was washed, dried, and then calcined in air at 450 $^\circ\text{C}$ for 8 h for SDA removal. Figure S2 shows the scanning electron microscopic (SEM) pictures of the surface and fractured cross-section of a typical zeolite membrane on the commercial tube support (MPT Inc. PA, USA). According to the observation on the cross-section SEM images, the zeolite membrane had a thickness of ~7 μm . The thermally activated tube membrane was modified by on-stream CCD of mono-silica in the 0.56 nm-diameter pores of the MFI zeolite crystals in the membrane layer using methyldiethoxysilane (MDES, Alfa Aesar) as the silica precursor. ^[3] The gas permeation and separation measurements were carried out on an apparatus that was described in the literature. ^[1]

References:

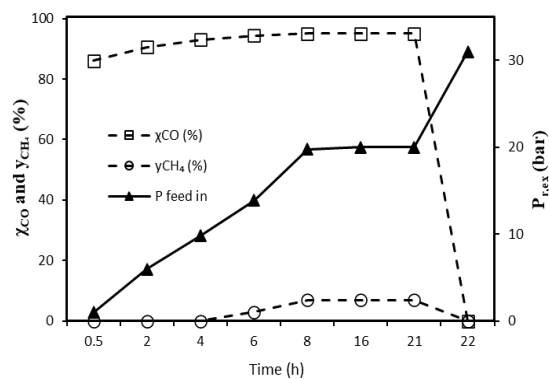
1. A. Arvanitis, X. Sun, S. Yang, D. Damma, P. Smirniotis, J. Dong, Approaching Complete CO Conversion and Total H_2 Recovery for Water Gas Shift Reaction in a High-Temperature and High-Pressure Zeolite Membrane Reactor. *J. Membr. Sci.* 549 (2018) 575–580.
2. X. Gu, Z. Tang, J. Dong, On-Stream Modification of MFI Zeolite Membranes for Enhancing Hydrogen Separation at High Temperature. *Micropor. Mesopor. Mater.* 111 (2008) 441–448.
3. Z. Tang, T.M. Nenoff, J. Dong, Internal Surface Modification of MFI-Type Zeolite Membranes for High Selectivity and High Flux for Hydrogen. *Langmuir* 25(9) (2009) 4848–4852.

Figure S1.

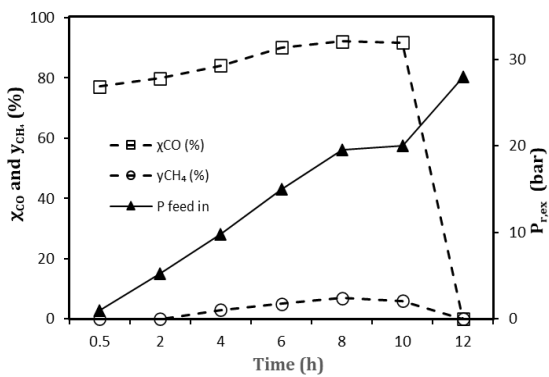
CO conversion and CH₄ content changes during the WGS reaction in the zeolite MR at 500°C as functions of time and pressure: (a) GHSV=15,000 h⁻¹ & $R_{S/CO}$ = 3.5, (b) GHSV=30,000 h⁻¹ & $R_{S/CO}$ = 3.5, (c) GHSV=15,000 h⁻¹ & $R_{S/CO}$ = 1.5.



(a)



(b)



(c)

Figure S2.

SEM and TEM images of the MWCNT tips growing on catalyst nanoparticles of various sizes during HTP WGS reaction in the zeolite MR: (a) SEM picture showing MWCNTs of different diameters, (b) TEM image showing catalyst particles in MWCNTs ends, (c) a growing tip on a catalyst particle of ~ 10 nm in size, (d) – (f) MWCNT tips on catalyst particles of different sizes and shapes.

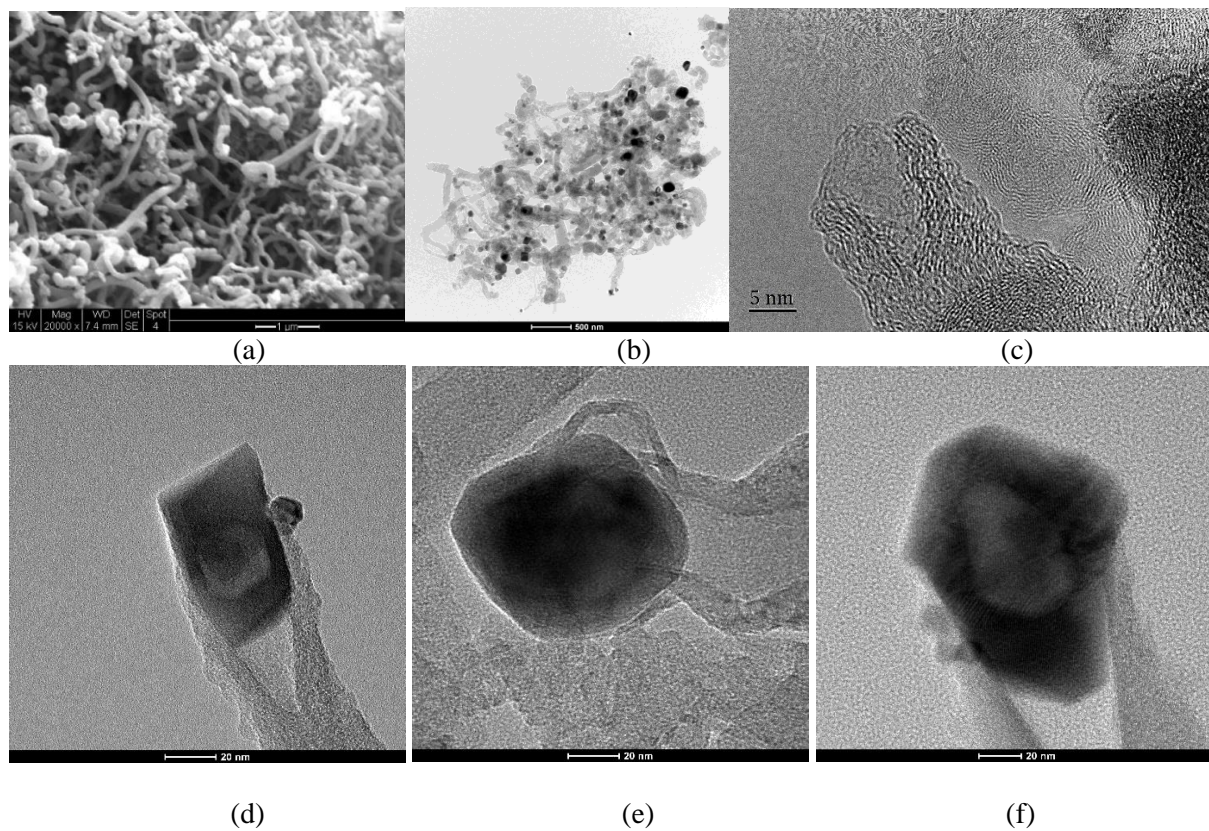
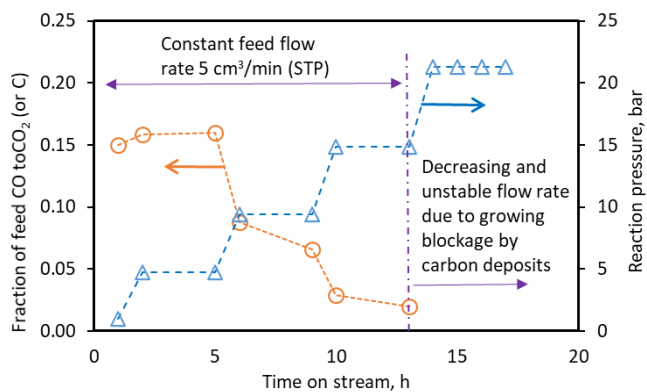
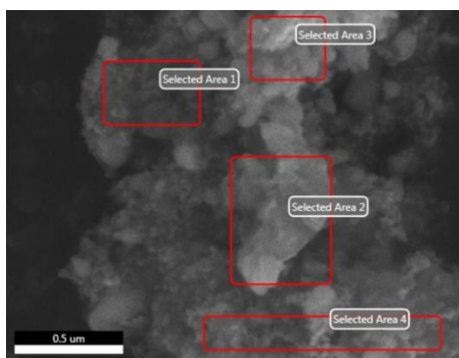


Figure S3.

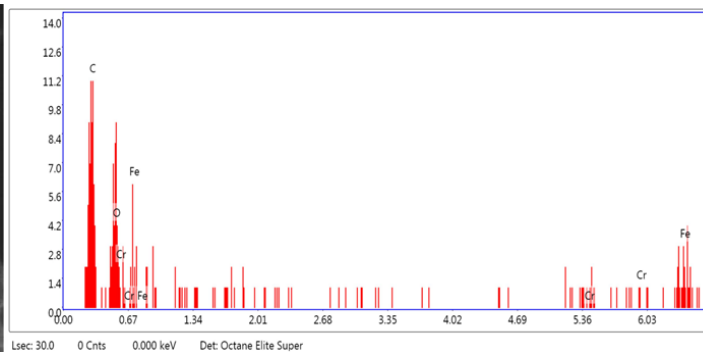
Results of pure CO feed reaction at 1.5 bar: (a) CO-conversion as a function of time and reaction pressure, (b) and (c) the SEM and EDS results of the solid products, and (d) and (e) TEM image showing graphitic carbon coating on catalyst and Raman shift spectrum of the carbon product.



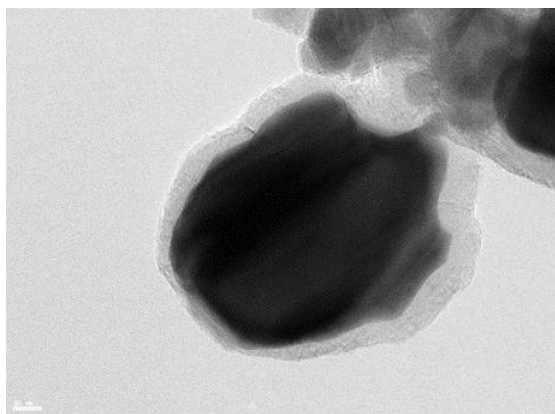
(a)



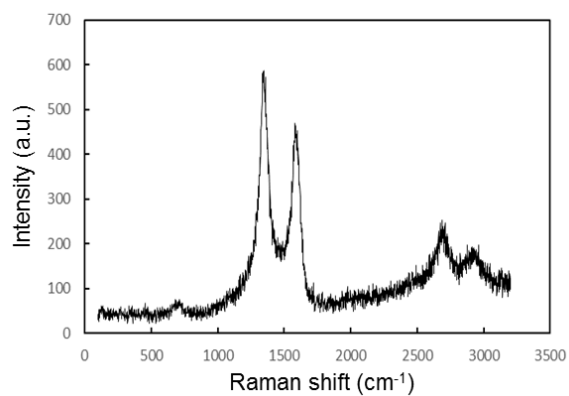
(b)



(c)



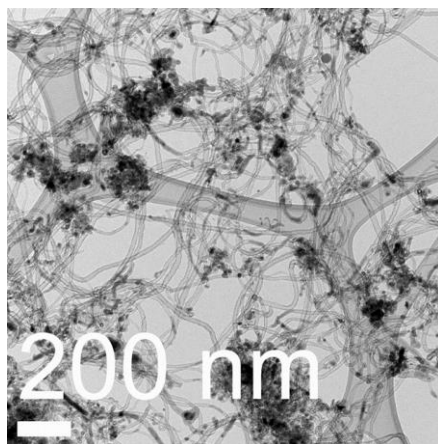
(d)



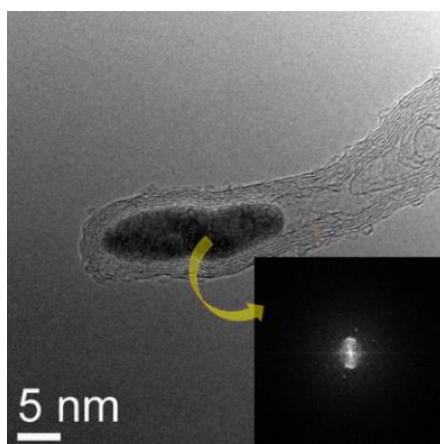
(e)

Figure S4.

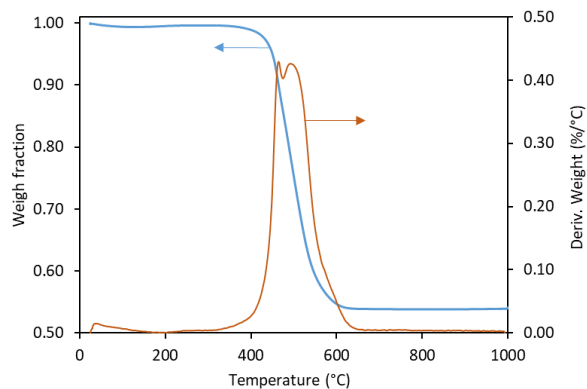
TEM and TGA examinations of the MWCNTs produced from a gas mixture of 80v.% CO + 20v.% CH₄ on the FeCr nanoparticle catalyst when reacting at 500°C and ambient pressure: (a) TEM image showing the uniformity of the long MWCNTs, (b) HR TEM image of a MWCNT tip containing a catalyst nanoparticle that appeared to be metallic Fe based on the electron diffraction pattern and EDS data, and (c) TGA/DTA results of the raw products containing MWCNTs, large catalyst particles, and supporting glass fibers.



(a)



(b)



(c)

Figure S5.

Results of SEM-EDS analysis for the MWCNT/Catalyst product from reaction of the CO/CH₄ mixture (80% CO+20% CH₄) containing 500 ppmv H₂S.

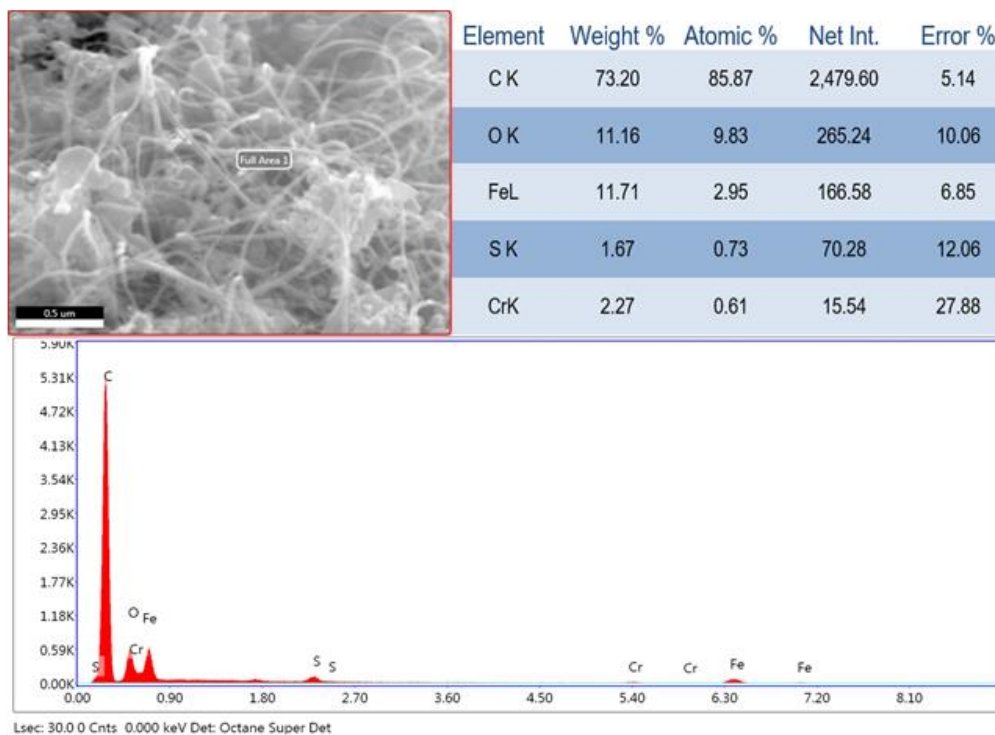
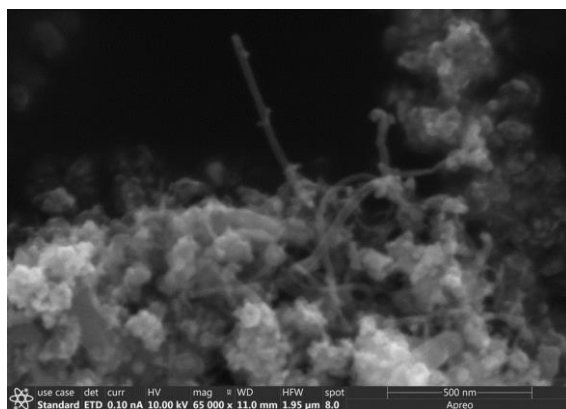
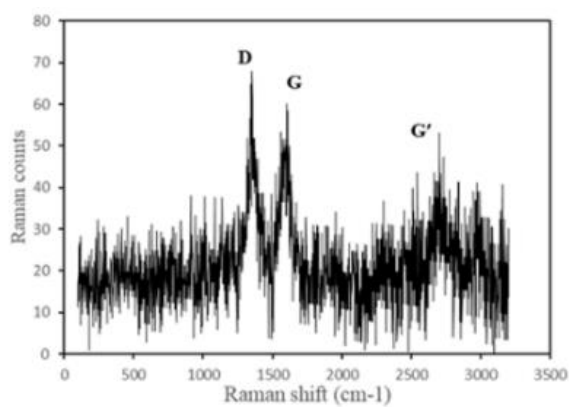


Figure S6.

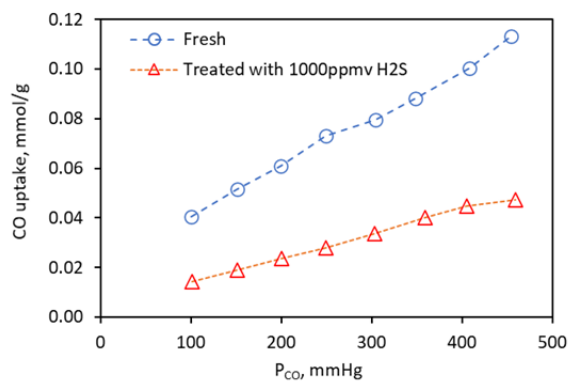
(a) The SEM picture of carbon product on the FeCr catalyst generated at 500°C and 1 bar from the feed of 80%CO+20%CH₄ with 800 ppmv H₂S, (b) Raman shift spectrum of the carbon product, and (c) CO chemisorption on fresh FeCr catalyst and on FeCr catalyst treated by 1000 ppmv H₂S in N₂ gas at 500°C for 5 h.



(a)



(b)



(c)

Figure S7

The EDS survey of the FeCr catalyst indicating a Fe:Cr atomic ratio of 11 ± 1.3 that agrees with the ratio in synthesis precursor ($\sim 10:1$).

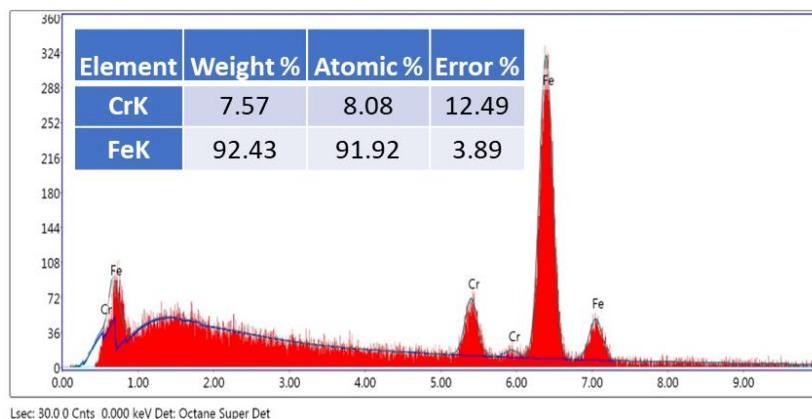
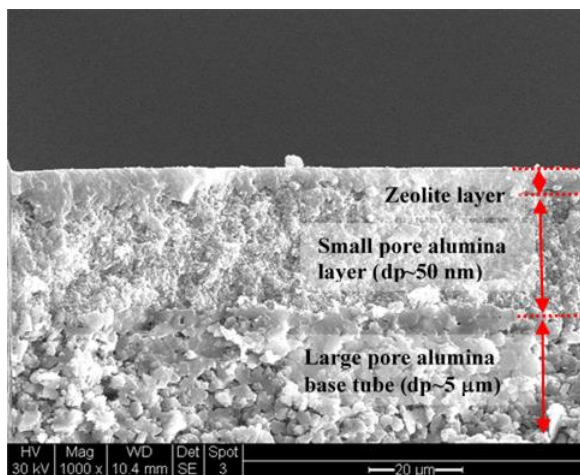
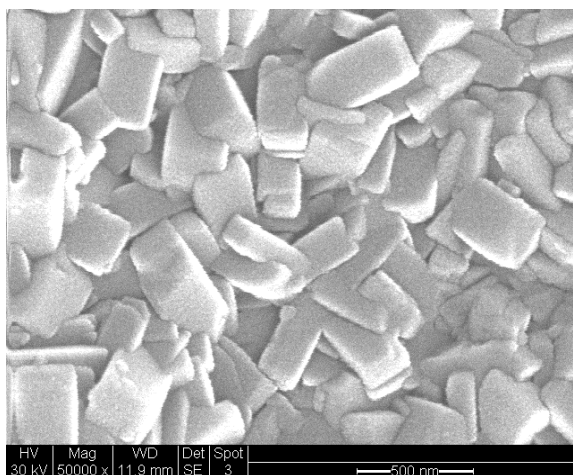


Figure S8.

The SEM pictures of the MFI-type zeolite membrane synthesized on the outer surface of the alumina tube: (a) fractured cross-section and (b) surface.



(a)



(b)