Electronic Supporting Information

FeN nanoparticles confined in carbon nanotubes for CO hydrogenation

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Experimental details

 Fe_2O_3 nanoparticles were introduced into CNTs (Chengdu Organic Chemicals, MFG code M12020702R) following our previously reported procedure.¹⁻³ More than 80% Fe_2O_3 nanoparticles were located inside the CNT channels. Fe_2O_3 -*in* was nitrided via temperature-programmed reaction method in ammonia atmosphere, adapted from a procedure reported earlier for bulk materials.⁴ Briefly, the sample was heated to a certain temperature and maintained for 2 h. After nitridation treatment, the sample was passivated in 1% O₂/He (20 ml/min) for 12 h before exposure to air. The resulting catalyst was labeled as Fe_xN -*in*-T, where T represents the nitridation temperature.

We also prepared an Fe_xN-*out* catalyst for comparison with Fe_xN particles dispersed on the exterior walls of CNTs. Fe₂O₃ particles were first deposited on the exterior walls with a precipitation-deposition method using Fe(NO₃)₃ and ammonia as the precursors. Following drying at 60 °C and treatment at 350 °C in Ar, the sample was subjected to the same nitridation treatment procedure as Fe_xN-*in*. In addition, Fe-*in* was prepared by reducing the CNT-confined Fe₂O₃ directly in H₂ for 6 h at $350 \degree C$.³

Inductively coupled plasma atomic emission spectrometry (ICP-AES, SHIMADZU ICPS-8100) analysis showed that Fe₂O₃-*in* had an iron loading of 5.61 wt% and Fe₂O₃-*out* of 5.24 wt%. Transmission electron microscopy (TEM) was carried on a FEI Tecnai G² microscope at an accelerating voltage of 120 kV. X-ray diffraction (XRD) was measured on a Rigaku D/Max 2500 diffractometer with a Cu K α (λ =1.541 Å) monochromatic radiation source. Some samples were also measured at the BL14B1 beamline (λ =1.2398 Å) of the Shanghai Synchrotron Radiation Facility (SSRF). ⁵⁷Fe Mössbauer spectroscopy analysis was conducted on a Topologic 500A spectrometer with a proportional counter. ⁵⁷Co(Rh) was used as the radioactive source and the Doppler velocity of the spectrometer was calibrated with an α -Fe foil. The spectra were fitted with appropriate superpositions of Lorentzian lines using the MossWinn 3.0i program.

CO hydrogenation was carried out in a fixed bed microreactor at 300 °C, 5 bar and a gas hourly space velocity (GHSV) of 15000 h⁻¹ (based on the volume of syngas passed through per volume of the catalyst per hour). A H₂/CO/Ar mixture (47.5/47.4/5.1 vol.%, purity of 99.99%) was taken as the feeding gas with Ar as an internal standard. 100mg catalyst was loaded into the reactor and pre-treated *in-situ* for 2 h in syngas (1 bar) at 260 °C. All gas lines after the reactor were kept at 150 °C. The effluents were analyzed by an online GC (Agilent 7890A), which was equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Four chromatography columns were installed, i.e. Porapak Q and 5 Å molecular sieves packed columns, and modified Al₂O₃ and FFAP capillary columns.



Figure S1 TEM images of the Fe₂O₃-*in* catalyst taken at different tilt angles: (a) $\alpha = -10^{\circ}$, $\beta = 0^{\circ}$; (b) $\alpha = 0^{\circ}$, $\beta = 0^{\circ}$; (c) $\alpha = 10^{\circ}$, $\beta = 0^{\circ}$; (d) $\alpha = 15^{\circ}$, $\beta = 0^{\circ}$; (e) $\alpha = 0^{\circ}$, $\beta = -5^{\circ}$; (f) $\alpha = 0^{\circ}$, $\beta = -10^{\circ}$. The images taken at different tilt angles indicate that most of the Fe₂O₃ nanoparticles of Fe₂O₃-*in* catalyst are located inside the channel of CNTs.



Figure S2 TEM images of the Fe₂O₃-*out* catalyst taken at different tilt angles: (a) $\alpha = -10^{\circ}$, $\beta = 0^{\circ}$; (b) $\alpha = 0^{\circ}$, $\beta = 0^{\circ}$; (c) $\alpha = 10^{\circ}$, $\beta = 0^{\circ}$; (d) $\alpha = 20^{\circ}$, $\beta = 0^{\circ}$; (e) $\alpha = 0^{\circ}$, $\beta = 5^{\circ}$; (f) $\alpha = 0^{\circ}$, $\beta = -10^{\circ}$. From the images taken at different tilt angles we did not observe Fe₂O₃ nanoparticles of Fe₂O₃-*out* inside the CNT channels.



Figure S3. TEM images of CNT-supported iron nitride prepared at different nitridation temperatures.



Figure S4. XRD patterns of CNT supported iron nitride prepared at different nitridation temperatures (a) Fe_xN -*in* and (b) Fe_xN -*out*.

| Sample | Subspectra | IS ^a | QS ^b | Hc | %Area ^d | Assignment |
|------------------------------------------------------|------------------------------|-----------------|-----------------------|------------|--------------------|----------------------------------------------|
| | | (mm/s) |) (mm/s) | (T) (| | |
| Fe _x N- <i>in</i> - 450 | Fe-I | 0.08 | 0 | 0 | 14 | γ''-FeN |
| 150 | Fe-II | 0.32 | 0.92 | 0 | 86 | γ "- or γ "-FeN with vacancies |
| Fe _x N- <i>out</i> - 400 | Fe-I | 0.06 | 0 | 0 | 21 | γ''-FeN |
| | Fe-II | 0.32 | 0.82 | 0 | 69 | γ "- or γ "-FeN |
| | Fe-III | 0.41 | 0.27 | 0 | 10 | ζ -Fe ₂ N |
| ^a Isomer shif ^d Uncertainty | t relative to is $\pm 5\%$. | α-Fe. | ^b Electric | quadrupole | splitting. | ^c Magnetic field. |

Table S1. Fitting parameters for the ⁵⁷Fe Mössbauer spectra in Figure 1e.

Table S2. Fitting parameters for the ⁵⁷Fe Mössbauer spectra in Figure 2b.

| Sample | e Sı | ubspectra | l | IS ^a | QS^{b} | | QS ^b | | QS ^b H ^c | | [^c | %Area ^d | | ead | Assignment | |
|-----------------------------------------|-------|-----------|----|-----------------|-------------------|-------|-----------------|-------|--------------------------------|---------|----------------|--------------------|-------------------|---------------------------------|------------|--|
| | | | | (mm/s) | | (mm/ | s) | (] | [) | | | | | | | |
| Fe _x N- <i>in</i> 450 | - | Fe-I | | 0.22 | | 0.05 | 5 | 15 | .9 | | 22 | | Fe ₂ C | x _x N _{1-x} | | |
| | | Fe-II | | 0.34 | | 0.99 |) | (|) | | 74 | | FeC | _x N _{1-x} | | |
| | | Fe-III | | 0.09 | | 0 | | (|) | | 4 | | γ"- | FeN | | |
| Fe _x N- <i>ou</i> 400 | t- | Fe-I | | 0.23 | | 0.02 | 2 | 15 | .9 | | 44 | | Fe ₂ C | x _x N _{1-x} | | |
| | | Fe-II | | 0.31 | | 1.08 | 3 | (|) | | 49 | | FeC | _x N _{1-x} | | |
| | | Fe-III | | 0.09 | | 0 | | (|) | | 7 | | γ"- | FeN | | |
| ^a Isomer | shift | relative | to | α-Fe. | ^b Elee | etric | quad | lrupo | le | splitti | ng. | °Mag | netic | field. | | |
| ^d Uncertainty is $\pm 5\%$. | | | | | | | | | | | | | | | | |



Figure S5. Room temperature ⁵⁷Fe Mössbauer spectra of 10% Fe_xN/SiO₂. Nitridation was carried out in ammonia at 500 °C via the same temperature-programmed reaction method as CNTs supported iron nitride catalysts. The isomer shift (IS) is 0.33 mm/s, the quadrupole splitting (QS) is 0.44 mm/s and the iron species exist as ϵ -Fe_{2.1}N in Fe_xN/SiO₂.

Table S3. Catalytic performance of 10%Fe₂N/SiO₂ catalyst in CO hydrogenation^a

| Activity | CO_2 | СН | Product distribution (mol%) | | | | | | |
|-----------------------------------------------------------------------------------------------------------------------|--------|------|-----------------------------|-------------------|---------------------------------------|-------------|--|--|--|
| $(\mu mol_{CO} s^{-1} g^{-1}{}_{Fe})$ | sel. | sel. | CH ₄ | $C_2^{=}-C_4^{=}$ | $(C_2^{=}-C_4^{=})/(C_2^{0}-C_4^{0})$ | C_{5}^{+} | | | |
| 75.6 | 40.5 | 58.3 | 30.5 | 42.4 | 2.8 | 11.7 | | | |
| ^{<i>a</i>} Reaction condition: 300°C, 5bar, H ₂ /CO/Ar (47.5/47.4/5.1), GHSV=15000h ⁻¹ | | | | | | | | | |

References

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