

Self-healing Catalysts: Co₃O₄ Nanorods for Fischer-Tropsch Synthesis

Cun Wen,^{a,b} Darrius Dunbar,^a Xin Zhang,^c Jochen Lauterbach,^{a,b} Jason Hattrick-Simpers^{a,b,*}

Experimental details:

Synthesis of Co₃O₄ nanorods and nanoparticles. The Co₃O₄ nanorods were synthesized according to literature reports.^(1, 2) Typically, 4.98g Co(OAc)₂·4H₂O was added to 60 mL of ethylene glycol and stirred until it dissolved. Then the solution was heated up to 160 °C under N₂ flow. After the temperature was stabilized, 200 mL 0.2 mol L⁻¹ Na₂CO₃ aqueous solution was pumped into the solution at the speed of 1.11 mL min⁻¹. After Na₂CO₃ solution dosing, the mixture was heated for one more hour at 160 °C. Then the product was collected by filtering and washed with ethanol. The filtered cake was then dried at 50 °C under vacuum overnight. After drying, the product was calcinated at 450 °C for 4h, which produced the final Co₃O₄ nanorods. For the synthesis of Co₃O₄ nanoparticles, the reaction temperature was changed from 160 °C to 80 °C and the other parameters were kept the same.

Fischer-Tropsch synthesis. 0.8 g Co₃O₄ nanorods or nanoparticles were reduced at 500 °C under pure hydrogen flow at 100 mL min⁻¹ for 5h before beginning Fischer-Tropsch synthesis (FTS). After reduction, the system was cooled down to 270 °C under hydrogen flow, and then gas was switched to syngas (31%CO, 62% H₂, and 7% Ar). The GHSV on the nanoparticles was maintained at 3,000 mL h⁻¹ g⁻¹ while the GHSV on the nanorods was varied from 3,000 mL h⁻¹ g⁻¹ to 32,000 mL h⁻¹ g⁻¹. The FTS was run at a reaction temperature of either 150 °C or 270 °C, and the pressure was maintained at 10 bar with a backpressure valve (GO regulator BP3-1A11Q5J111). All the downstream lines after FTS reactors were kept above 160 °C including the back pressure valve and the injection valve on the gas chromatograph (GC). The products from FTS were analyzed on-line with a Shimadzu GC 2014 equipped with both thermoconductivity and flame ionization detectors. Two columns were employed in the GC, one was a packed column (Heysep D) for analyzing CO, CO₂, and C1 to C6, and the other was a capillary column (ZB-1 HT) for analyzing all hydrocarbons. The hydrocarbon selectivity was calculated on a carbon basis. After several hours of dry syngas reactions, water was dosed into the system with a high performance liquid chromatograph (HPLC) pump (Alltech 426) at rate of 0.01 mL min⁻¹ to examine the resistivity of nanorods and nanoparticle to the water oxidation.

In situ Raman. *In situ* Raman was conducted using a 632.81 nm wavelength laser. The *in situ* Raman experiment started with a H₂ temperature programmed reduction (TPR), from room temperature to 500 °C at a ramping rate of 5 °C min⁻¹. After reaching 500 °C, the sample was reduced at this temperature for 3 hours. Then the system was cooled down to 270 °C, and the gas was switched to syngas (31%CO, 62% H₂, and 7% Ar) at 1 bar. After several hours of dry syngas feeding, 25 vol% water was added to the feed, consistent with the feed used during FTS reactions.

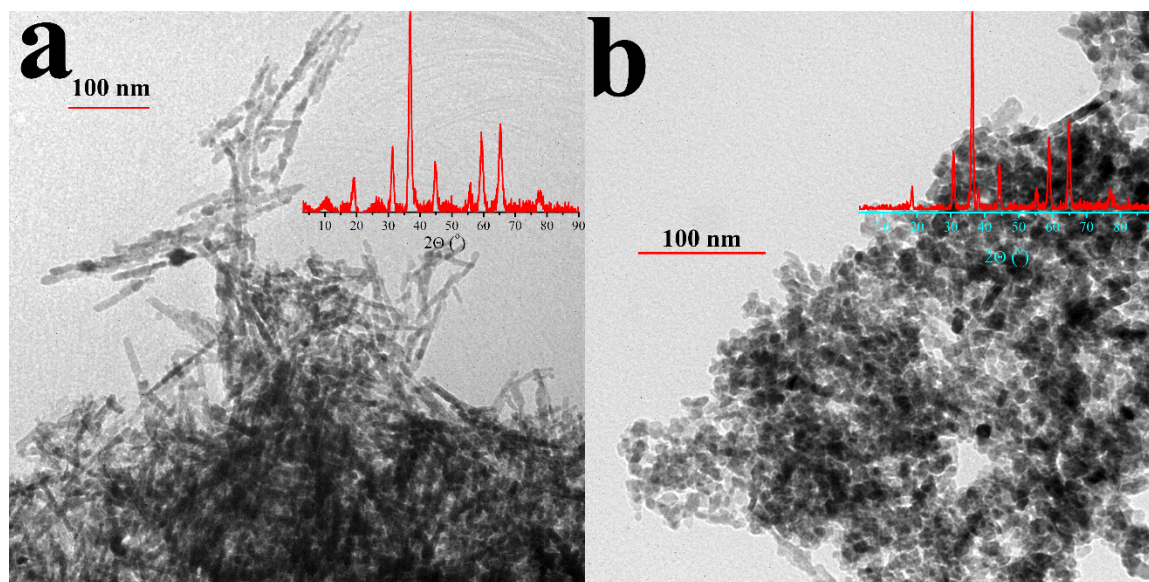


Figure S1. TEM images of Co a) nanorods and b) nanoparticles. Insets in a) and b) are the corresponding XRD patterns of nanorods and nanoparticles, respectively.

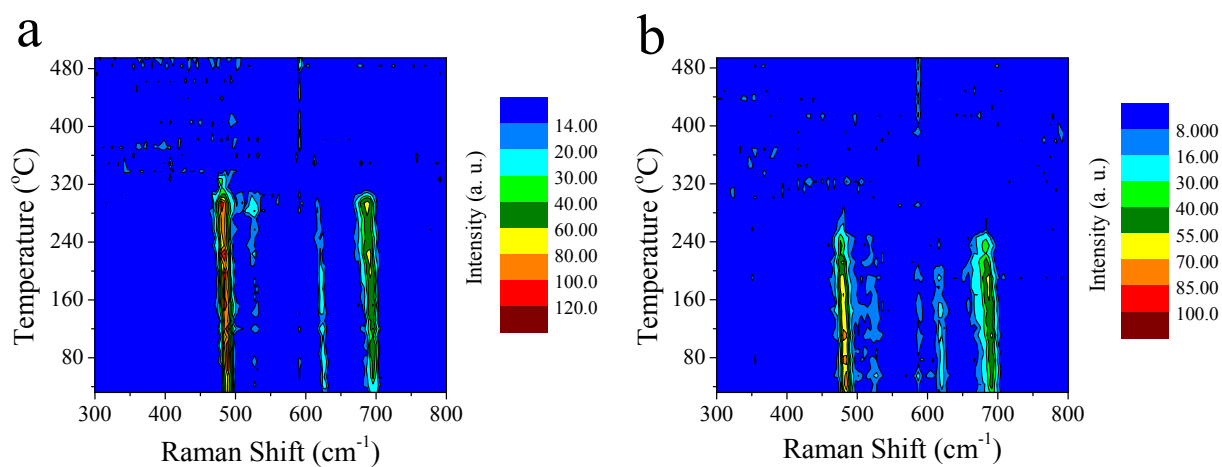


Figure S2. *in situ* Raman spectra of a) nanoparticles and b) nanorods during hydrogen temperature programmed reduction.

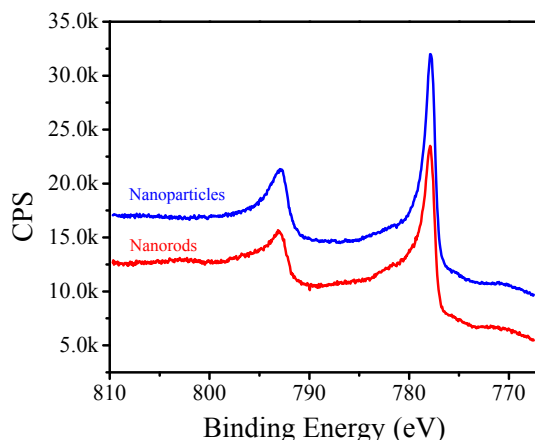


Figure S3. XPS profiles of Co 2p on Co nanoparticles and nanorods after reduced at 773 K for 5 hours.

An alternative method of decreasing the CO conversion is to increase the gas hour space velocity (GHSV) during FTS (Fig. S4). Here it was observed that as the GHSV increased, the CO conversion and CO₂ selectivity decreased and the C₅₊ selectivity increased. Previous FTS studies have shown that product selectivity is related to the coverage of surface species, and increasing CO coverage at the expense of H₂ coverage will increase the C₅₊ selectivity.(3, 4) We hypothesize here that the difference in the sticking coefficients of CO (0.9-1.0) and H₂ (0.04-0.08) leads to an increase in the relative coverage of CO at higher space velocities and a consummate increase in C₅₊ selectivity.(5, 6) Despite the change in surface coverage, no significant water effect on the FTS performance of Co nanorods is observed at GHSVs of 9,333h⁻¹ and 18,666 h⁻¹. Upon further increasing the GHSV to 32,000 h⁻¹, a slight change in the conversion and CO₂ selectivity was observed in the FTS performance of the nanorods during water dosing. The CO conversion increased from 12 ±3% to 15 ±5% and CO₂ selectivity from 1% to 9 ±2%. This effect is, however, negligible compared to the changes observed on the nanoparticles.

The effect of water on the FTS performance at high GHSV (32,000 h⁻¹) can be attributed to the changes in surface coverage of CO and H₂. A higher coverage of CO and lower coverage of H₂ would tend to promote the WGS reaction.(7) A similar effect on catalytic performance during water dosing at high space velocity has also been observed in NO reduction by CH₄.(8) The similarities can be expected as the reactants share common molecular structures. Both the NO and CO have σ and π bonds, and the chemical adsorption process involves electron transfer from the σ bonds of CO and NO to the metal, which then back-donates electrons to the π bond. The similarity in bond structure and adsorption interaction leads to similar sticking coefficients for CO (0.9-1.0) and NO (1.0).(5, 9) On the other hand, H₂ and CH₄ have only σ bonds, which lead to a lower sticking coefficient (0.04-0.08 for H₂ and <0.001 for CH₄) compared with CO and NO.(10)

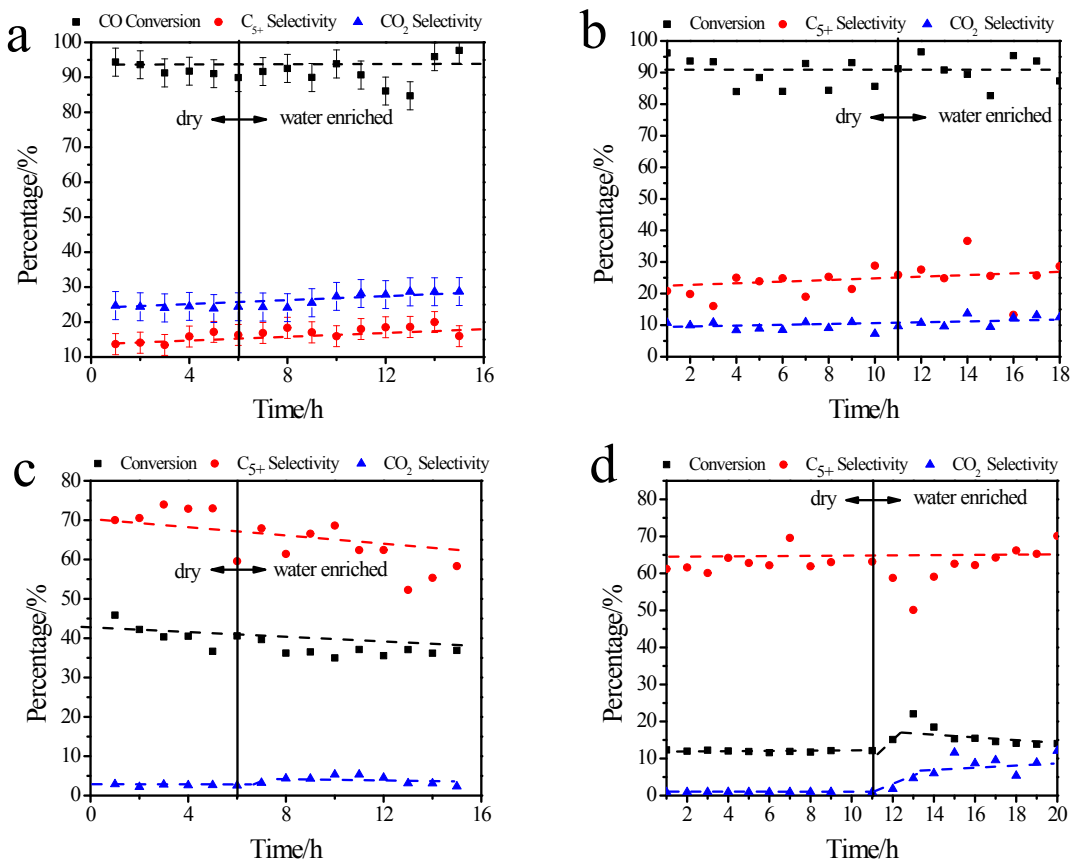


Figure S4. Fischer-Tropsch synthesis (FTS) on nanorods at different gas hour space velocity (GHSV) a) 3,000 h⁻¹; b) 9,167 h⁻¹; c) 18,333 h⁻¹; d) 32,000 h⁻¹. The dashed lines were added as a guide to the eyes. Except GHSV, the Rest of the reaction conditions are the same to Fig. 2a.

	CO Conversion	C ₅₊ Selectivity	CO ₂ Selectivity
Nanoparticles (dry feed, T _{reaction} = 543 K, GHVS = 3000 h ⁻¹)	5% ± 1%	31% ± 2%	14% ± 2%
Nanoparticles (water feed, T _{reaction} = 543 K, GHVS = 3000 h ⁻¹)	13% ± 3%	15% ± 2%	65% ± 4%
Nanorods (dry feed, T _{reaction} = 433 K, GHVS = 3000 h ⁻¹)	12% ± 2%	4% ± 1%	40% ± 3%
Nanorods (water feed, T _{reaction} = 433 K, GHVS = 3000 h ⁻¹)	12% ± 2%	4% ± 1%	40% ± 3%
Nanorods (dry feed, T _{reaction} = 543 K, GHVS = 3,000 h ⁻¹)	94% ± 4%	14% ± 3%	25% ± 4%
Nanorods (water feed, T _{reaction} = 543 K, GHVS = 3,000 h ⁻¹)	94% ± 4%	18% ± 3%	28% ± 4%

Nanorods (dry feed, $T_{\text{reaction}} = 543 \text{ K}$, GHVS $= 9,167 \text{ h}^{-1}$)	$90\% \pm 6\%$	$10\% \pm 2\%$	$25\% \pm 8\%$
Nanorods (water feed, $T_{\text{reaction}} = 543 \text{ K}$, GHVS $= 9,167 \text{ h}^{-1}$)	$90\% \pm 6\%$	$10\% \pm 2\%$	$25 \pm 8\%$
Nanorods (dry feed, $T_{\text{reaction}} = 543 \text{ K}$, GHVS $= 18,333 \text{ h}^{-1}$)	$40\% \pm 4\%$	$71\% \pm 2\%$	$3\% \pm 1\%$
Nanorods (water feed, $T_{\text{reaction}} = 543 \text{ K}$, GHVS $= 18,333 \text{ h}^{-1}$)	$37\% \pm 4\%$	$62\% \pm 5\%$	$5\% \pm 2\%$
Nanorods (dry feed, $T_{\text{reaction}} = 543 \text{ K}$, GHVS $= 32,000 \text{ h}^{-1}$)	$12\% \pm 2\%$	$62\% \pm 3\%$	$1\% \pm 1\%$
Nanorods (water feed, $T_{\text{reaction}} = 543 \text{ K}$, GHVS $= 32,000 \text{ h}^{-1}$)	$14\% \pm 2\%$	$64\% \pm 4\%$	$9\% \pm 2\%$

Table S1.) Summary of nanorod and nanoparticle FTS performance before and after water addition to the feed.

1. X. W. Xie, Y. Li, Z. Q. Liu, M. Haruta, W. J. Shen, Low-temperature oxidation of CO catalysed by Co₃O₄ nanorods. *Nature* **458**, 746-749 (2009)10.1038/nature07877).
2. X. Xie, P. Shang, Z. Liu, Y. Lv, Y. Li, W. Shen, Synthesis of Nanorod-Shaped Cobalt Hydroxycarbonate and Oxide with the Mediation of Ethylene Glycol. *The Journal of Physical Chemistry C* **114**, 2116-2123 (2010)10.1021/jp911011g).
3. J. Chen, Z. P. Liu, Origin of selectivity switch in Fischer-Tropsch synthesis over Ru and Rh from first-principles statistical mechanics studies. *J Am Chem Soc* **130**, 7929-7937 (2008); published online EpubJun 25 (10.1021/ja7112239).
4. J. P. den Breejen, P. B. Radstake, G. L. Bezemer, J. H. Bitter, V. Froseth, A. Holmen, K. P. de Jong, On the Origin of the Cobalt Particle Size Effects in Fischer-Tropsch Catalysis. *J Am Chem Soc* **131**, 7197-7203 (2009); published online EpubMay (10.1021/ja901006x).
5. M. E. Bridge, C. M. Comrie, R. M. Lambert, Chemisorption studies on cobalt single crystal surfaces: I. Carbon monoxide on Co(0001). *Surf Sci* **67**, 393-404 (1977).
6. M. E. Bridge, C. M. Comrie, R. M. Lambert, Hydrogen chemisorption and the carbon monoxide-hydrogen interaction on cobalt (0001). *J Catal* **58**, 28-33 (1979).
7. A. A. Gokhale, J. A. Dumesic, M. Mavrikakis, On the Mechanism of Low-Temperature Water Gas Shift Reaction on Copper. *J Am Chem Soc* **130**, 1402-1414 (2008)10.1021/ja0768237).
8. Y. J. Li, P. J. Battavio, J. N. Armor, Effect of Water Vapor on the Selective Reduction of NO by Methane over Cobalt-Exchanged ZSM-5. *J Catal* **142**, 561-571 (1993); published online Epub8// (<http://dx.doi.org/10.1006/jcat.1993.1231>).
9. T. Vaara, J. Lahtinen, P. Hautojärvi, Reactions of CO and NO on Mg promoted cobalt. *Applied Surface Science* **89**, 103-111 (1995); published online Epub6// ([http://dx.doi.org/10.1016/0169-4332\(95\)00038-0](http://dx.doi.org/10.1016/0169-4332(95)00038-0)).

10. H. Burghgraef, A. P. J. Jansen, R. A. van Santen, Electronic structure calculations and dynamics of methane activation on nickel and cobalt. *The Journal of Chemical Physics* **101**, 11012-11020 (1994)doi:<http://dx.doi.org/10.1063/1.467852>.