A Novel Nano Fischer-Tropsch Catalyst for the Production of Hydrocarbons

Guanqun Luo[1], Armando G. McDonald[1], Blaise-Alexis Fouetio Kengne[2], and David N. McIlroy[2]

[1]Dept of Forest, Rangeland & Fire Sciences, [2]Dept of Physics, University of Idaho, Moscow ID 83844-1132

Introduction

Due to the serious environmental issues caused by utilization of fossil fuels and finite oil reserves, alternative sources of sustainable fuels and chemicals are required. FTS provides a method with which to convert carbon-containing feedstock, like biomass, into clean fuels and valuable chemicals via synthesis gas (syn-gas).

A catalyst support not only works as a carrier, but also contributes to the performance of the catalyst. An optimal support should be chemically inert, mechanically and thermally stable, with a high solvent-accessible surface area, and balanced metal-support interaction. Within this scenario, a novel material, silica nanosprings (NS) meets all of the above criteria for FTS catalyst. In the present study, Co decorated silica NS-FTS catalyst (Co/SiO_2-NS) were evaluated. The physico-chemical properties of the catalyst were characterized and the catalytic performance was evaluated in a micro-reactor. The results are compared with a conventional silica gel-supported Co catalyst (Co/SiO_2-gel).

Experimental

Materials

- Co/SiO_2-gel precursor $Co(NO_3)_2$ dissolved in water and vacuum impregnated into gel and calcined at 400°C .
- Co/SiO_2-NS precursor $Co(C_5H_7O_2)_2$ dissolved in ethanol and added to NS coated quartz frit (10 mm) support and heated to 500°C in Ar/H_2.

Catalyst characterization

- SEM (Leo Supra 35) and TEM (Jeol JEM-2010) analysis
- X-Ray diffraction (XRD, Siemens D5000)
- H_2 Temperature programmed reduction (TPR) Micromereritcis AutoChem II 2920
- X-ray photoelectron spectroscopy

Catalyst evaluation

- FTS was performed using a quartz fix-bed micro-reactor (1/2" x 14") (Fig. 1). The catalyst (200 mg Gel and 5 mg NS) and reduced in H_2 at 400°C for 12 h. The FTS reactions were carried out at 230°C with a H_2/CO (2:1) at 60 mL/min and 10 mL/min N_2. Products were collected in 3-stage impinger trap in liquid N_2.
- Collected hydrocarbons were analyzed by GC-MS (Focus-ISQ) on a RTx-5ms (0.25 mm x 30 m) column (40-250°C at 5°C/min).
- Gas samples were analyzed by GC-TCD (Gow-Mac 350) using a HaySep DB column (3 mm x 9.1 m) at 30°C.

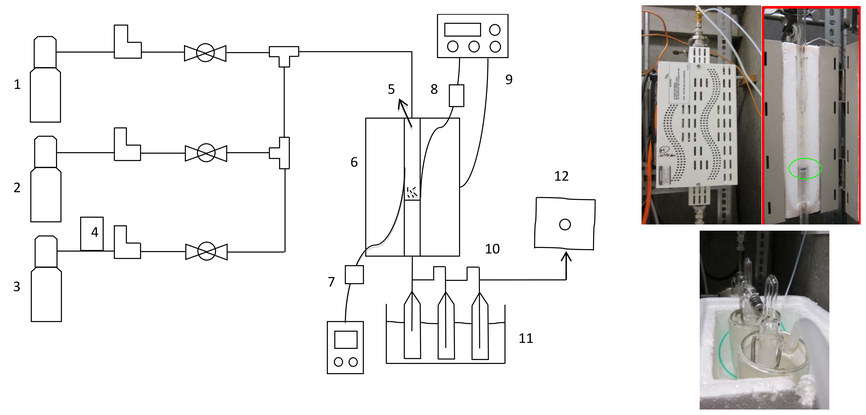


Fig. 1. Reactor set-up (1) CO; (2) H_2; (3) N_2; (4) mass flow controllers; (5) quartz tube reactor; (6) furnace; (7) thermometer; (8) J-thermocouple; (9) temperature controller; (10) 3-stage condenser; (11) liquid N_2 bath; (12) gas sampling bag.

Results

Initial catalyst characterization

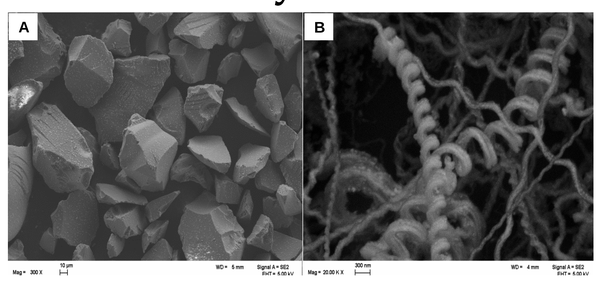


Fig. 2. SEM of (A) SiO_2-gel support and (B) nanospring (NS) support

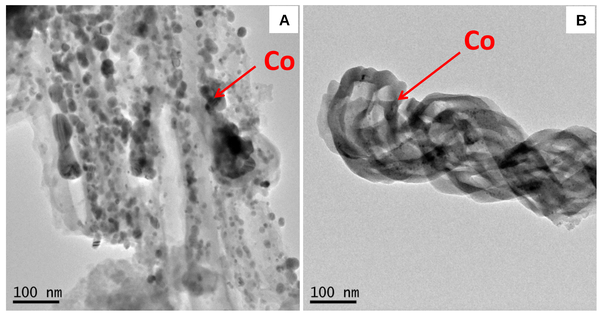
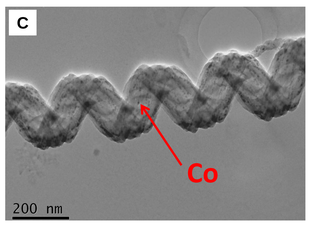


Fig. 3. TEM of (A) Co/SiO_2-gel and (B and C) Co/SiO_2-NS



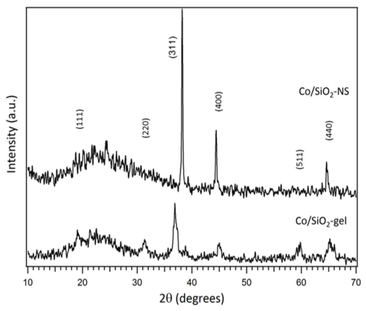


Fig. 4. XRD diffractogram of Co/SiO_2-gel and Co/SiO_2-NS

Table 1. BET surface area, porosity, Co_3O_4 crystallite size of supports and Co decorated catalysts

Support-catalyst	BET area ($m^2\ g^{-1}$)	pore volume ($cm^3\ g^{-1}$)	Co_3O_4 size by TEM (nm)	Co_3O_4 size by XRD (nm)
SiO_2-gel	478	0.82	--	--
SiO_2-NS	329	0.42	--	--
Co/SiO_2-gel	370	0.62	14.7	13.1
Co/SiO_2-NS	208	0.29	4.5	12.7

- The NSs have an open structure making it very accessible to gases.
- Co/SiO_2-NS had small Co nanoparticles (by TEM) on the surface than the Co/SiO_2-gel

Catalyst evaluation

- Products were identified by GC-MS (Fig. 5) and GC-TCD (Fig. 6) as hydrocarbons (C_1-C_{18}).
- Obtained max CO conversions of 85% for Co/SiO_2-gel and 66% for Co/SiO_2-NS.
- Need to determine why the low conversions for Co/SiO_2-NS.

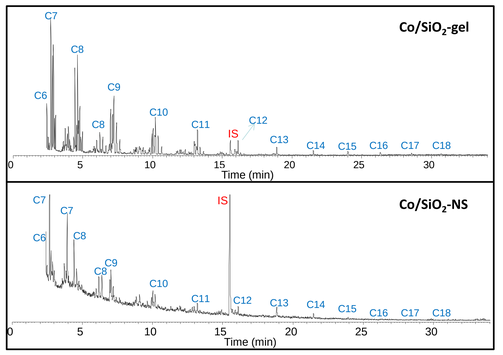


Fig. 5. GC-MS chromatograms of FTS products from Co/SiO_2-gel and Co/SiO_2-NS catalysts

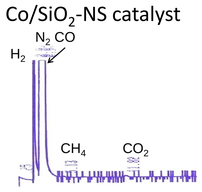


Fig. 6. GC-TCD chromatogram of gaseous FTS products from Co/SiO_2-NS catalyst

Further catalyst characterization

- H_2-TPR analysis showed that the Co on SiO_2-NS was not reduced at 400°C and requires a higher activation temperature of 603°C than 325°C for Co/SiO_2-gel (Fig. 7).
- XPS analysis of Co/SiO_2-NS shows that Co was not fully reduced to Co^0 at 400°C and explains low conversion (Fig. 8).

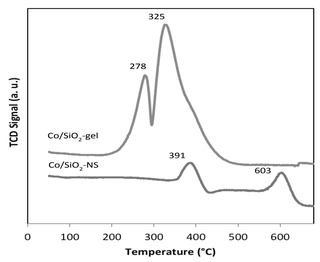


Fig. 7. H_2-TPR of Co/SiO_2-gel and Co/SiO_2-NS catalysts

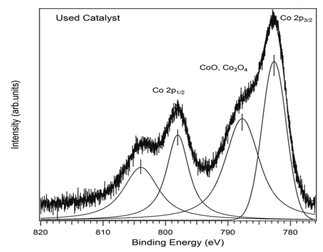


Fig. 8. XPS spectrum of Co/SiO_2-NS catalyst

Conclusions

- Novel silica Co-NS FTS catalyst was successfully prepared.
- The Co/SiO_2-NS unique morphology of highly accessible surface had good FTS activity even though not fully reduced.
- Ongoing work is focused on (i) optimizing the preparation of the NS based catalysts, (ii) Co reduction, (iii) catalyst surface characterization, and (iv) other active metals.

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