

Fischer-Tropsch Synthesis with Iron Nano-catalyst

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Introduction

Use of iron catalysts in slurry-phase Fischer-Tropsch synthesis (FTS) has been limited by their high rate of attrition to ultrafine particles leading to high slurry viscosity and difficulty in wax/catalyst separation. Phase-transformation of iron catalyst during activation and FTS plays an important role to determine the structural integrity of the particles. Sequential phase-evolution from Fe₂O₃ to Fe₃O₄ and finally to iron carbides have been reported [1]. Reversible oxide/carbide transformation during FTS can induce stress into the particle because of significant difference in densities of the two phases and finally results in generation of ultrafine particles. Hence, re-oxidation of carbide phase during FTS has the potential to affect particle morphology and catalytic performance. Phase-composition, re-oxidation pattern and change in particle size of an iron nano-catalyst during carbidation and FTS has been studied.

Materials and Methods

A commercial, unpromoted ultrafine iron oxide catalyst (Mach I, 3-5 nm particle size, 250 m²/g surface area) was used. FTS experiments were conducted in a CSTR at 270 °C, 100 psig and a syngas SV of 3 sl/h/g catalyst. Catalyst samples withdrawn at increasing times are analyzed by HRTEM, EELS, STEM (JEOL JEM-2010F), and Mössbauer spectroscopy (MS-1200, Ranger Scientific; 30 mCi ⁵⁷Co in Rh matrix as radiation source).

Results and Discussion

Mössbauer results indicate that carbidation with CO at 270 °C for 24 h converts the initial Fe₂O₃ into a mixture of 85% χ -Fe₅C₂ and Fe₃O₄. The activated catalyst results in ca. 85% CO conversion (Figure 1a) which decreased to ca. 12% over 300 h of FTS time and thereafter remained nearly constant up to 600 h. Reoxidation of the carbide phase formed initially after carbidation continues with FTS and the catalytic activity closely follows the carbide content of the catalyst. HRTEM image (Figure 1b) of catalyst sample collected after 28.9 h of FTS reveals an inner oxide core (the d-spacing of 2.6 Å can correspond to high intensity [311] plane of Fe₃O₄) is surrounded by outer carbide region (the d-spacing of 2.0 Å can be assigned to high intensity [510] or [021] plane of χ -Fe₅C₂). The appearance of inner oxide core encapsulated by concentric carbide zone indicates that nucleation for carbide to oxide transformation initiates at the center of the particle which is under oxidizing environment (due to presence of FTS products like CO₂ and H₂O). Particle size distribution measurements suggest nano-scale growths of individual catalyst particle. Statistical average particle diameters ($d_{3,2}$ and $d_{4,3}$) are found to increase by a factor of 4 over 600 h of FTS (Table 1). Large particles with the largest dimension larger than 150 nm are also identified. Chemical compositions of the larger particles are found to be single crystal Fe₃O₄ as revealed by EELS-STEM analysis. An amorphous carbon rim of thickness 3-5 nm around some particles after activation and

during FTS is observed. Well ordered graphitic carbon layer on larger single crystal magnetite particles is also identified by EELS-STEM analysis. However the maximum thickness of the carbon (amorphous or graphitic) rim does not grow above 10 nm, suggesting that the growth of particles are not due to carbon deposition.

Table 1. Variation of particle size of iron nano-catalyst during FTS.

FTS Time, h	$d_{3,2}$ ($= \sum d_i^3 N_i / \sum d_i^2 N_i$), nm	$d_{4,3}$ ($= \sum d_i^4 N_i / \sum d_i^3 N_i$), nm
0	23.48	25.86
258.3	41.73	49.02
620.8	82.52	99.89

Significance

The FTS activity of unpromoted iron catalyst directly follows the carbide content of the catalyst. Gradual reoxidation of the carbide phase continues with FTS and the carbide to oxide phase transformation initiates at the center of the particles. Particle attrition is observed during FTS when large-sized iron catalyst particles are used. However, for nano-scale particles, growth of individual catalyst particles are found. The results suggest that carbide to oxide transformation and nano-scale growth of particles continues either in succession or at least simultaneously; but definitely not in the reverse order.

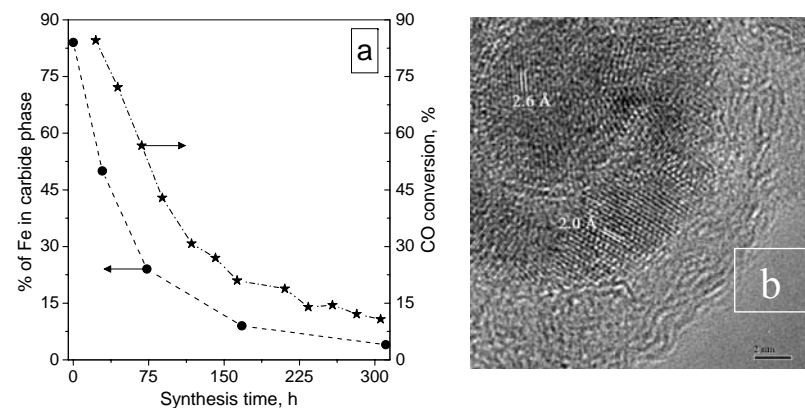


Figure 1. (a) Phase-composition of iron catalyst and CO conversion during FTS; (b) HRTEM image of catalyst after 28.9 h of FTS: an inner oxide core surrounded by outer carbide layer.

References

1. Davis, B. H. Technology Development for Iron Fischer-Tropsch Catalysis, US DOE Final Technical Report, Contract # DE-AC22-94PC94055-13 (1999).