# Direct visualization of carburization of Fe nanoparticles in synthetic gas: application of Environmental TEM for Fischer-Tropsch catalysis

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**Abstract:** Structural evolution of iron nanoparticles involving the formation and growth of iron carbide nuclei in the iron nanoparticle was directly visualized at the atomic level using environmental transmission electron microscopy under reactive conditions mimicking Fischer-Tropsch synthesis. Formation of the iron carbide nuclei and surface reconstruction of the iron nanoparticle play an essential role in carburization of the iron nanoparticle and consequent formation of Fe5C2. Identification of carbide and oxide intermediates evidenced by high-resolution TEM images, electron diffraction patterns and electron energy-loss spectra provides a detailed picture from initial activation to final degradation of iron under synthesis gas.

**Keywords:** Environmental TEM, Fischer-Tropsch synthesis, carbide

## 1. Introduction

Hydrogenation of CO by H2, known as Fischer-Tropsch synthesis (abbreviated as FTS) offers an attractive route to produce high quality fuels and chemicals via synthesis gas from coal, natural gas, or biomass. FTS is an essential step in coal-to-liquids (CTL) technology, and is of great interest in China as a clean process for the utilization of coal, and prevents the environmental pollution associated with direct combustion of coal in domestic life and in industry.[1] For 2017, Chinese CTL processes based on gasification and FTS are foreseen to account for a cumulative production capacity of over 4 million tons.1 Although FTS has been developed over 90 years, various key issues related to the activation of Fe catalysts and formation of iron carbides are still disputed.[2] However, present characterization techniques don’t allow directly probe changes in structure or chemical properties of an individual Fe nanoparticle under reaction conditions at the (sub) nanoscale and ex-situ work cannot reflect realistic chemical nature of activated Fe catalysts due to critical instability of metallic iron and iron carbide species. In order to identify the initial formation of the surface carbide species in Fe nanoparticles and record the carburization process at the nanoscale and under chemical conditions, an environmental transmission electron microscope (ETEM) equipped with aberration-correction was employed to characterize the structure and chemistry of individual iron nanoparticles at the atomic-level, under a reactive gaseous environment. Using this tool, reduction of iron oxide nanoparticles by H2 and subsequent carburization by syngas were studied with atomic spatial resolutions, the latter step has been regarded as a key activation step in FTS.

## 2. Results and discussion

Both reduction of FeOx and subsequent carburization of Fe were directly conducted in Cs-corrected Environmental TEM. A Fe nanoparticle of 20 nm prepared via the reduction of FeOx nanoparticles by H2 was chosen as a subject to carburization. In ETEM, carburization took place as the Fe nanoparticle was exposed to a mixture of CO and H2 with molar ratio of 1 to 4 at 280$^{o}$C with total pressure of 6.6 mbar. High-resolution images and corresponding FFT of the metallic nanoparticle before and after exposure to syngas clearly show appearance of more and more new crystalline atterns in the Fe nanoparticles under the gaseous atmosphere. After exposure to syngas for 40 minutes, both selected area Diffraction pattern and FFT confirms formation of Fe5C2 embedded into the iron nanoparticle. Comparing the FFTs related with the different reaction times (Figure 1), two sets of spots, An (n=1-5) and Bn (n=1-5) can be identified in all images, which both indicate similar d-spacings of about 2 Å. By applying masks to the spots An series, the resulting IFFTs correlated with the different reaction times in Figure 2 show dynamic information about the evolution of specific surface features of the nanoparticle under the reaction conditions.Clearly, the surface is dynamic, with features appearing and disappearing in minutes via, assumedly, surface reconstruction. We assume that these surface components are metastable carbidic phases. In contrast, a scene based on the IFFT images derived from the series Bn spots (Figure 2) shows gradual growth of discrete grains during the experiment. After 8 minutes of reaction, several small nuclei with diameters of about 1 nm formed in the central part of the nanoparticle, they quickly consolidated into one grain and grew up into a beltlike Fe5C2 component across the nanoparticle. After exposure to syngas for longer time, the nanoparticles did not carburize further, but underwent other side-reactions including oxidation and formation of coke. A newly formed Fe3O4 particle of 10 nm diameter was observed on top of the particle after 150 minutes' reaction (Figure 3a) and its oxidic nature is confirmed by the EEL spectrum (Figure 3c). It seems that, in the presence of an oxygen source (most likely H2O), iron atoms migrate out of the Fe- FeCx composite and bind to oxygen, resulting in the formation of the oxide adjacent to the iron particle. This also means that the oxidation might not rapidly deactivate the iron catalyst if it did not directly cover or destruct the Fe-Fe5C2 particle. Meanwhile, critical growth of graphite carbon was also observed.

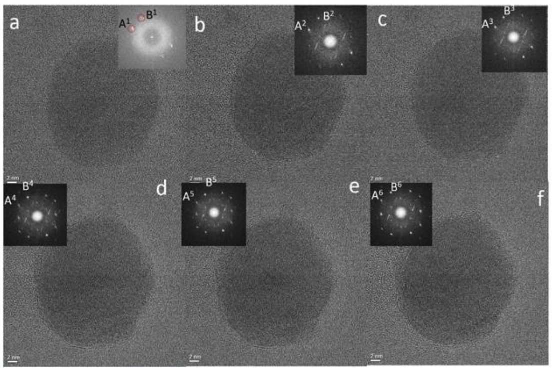

**Figure 1**. HRTEM image of the nanoparticle after introduction of CO for different time a) 8 minutes, b) 9 minutes, c) 12 minutes, d) 40 minutes, e) 42 minutes, f) 60 minutes, inset is corresponding FFT image with An and Bn marks.

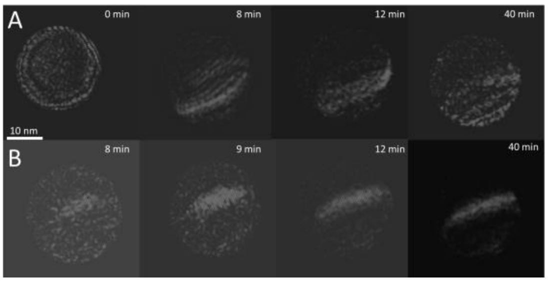

**Figure 2**. Upper a) Sequence A: masked IFFT images formed using a series A spots in the corresponding FFT images (Figure 1a-f), respectively; Lower b) Sequence B: masked IFFT images formed using a series B spots in the corresponding FFT images (Figure 1b-f),

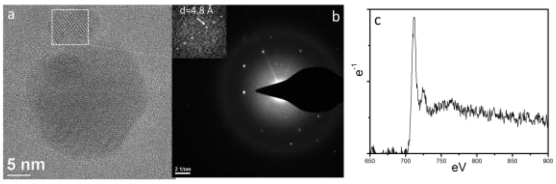

**Figure 3**. a) HRTEM image of the nanoparticle after 150 minutes' reaction and b) the corresponding SAED pattern, inset is FFT image of the boxed region in the HRTEM a), the dspacing of 4.8 Å corresponds to the (111) plane of Fe3O4, c) EELs Fe L2,3 edge collected from the center of the boxed region under STEM mode

## 3. Conclusions

Using environmental TEM, we directly visualized the evolution of a single metallic Fe nanoparticle at nanoscale resolution under conditions relevant for Fischer-Tropsch catalysis, in which carburization, oxidation, growth of nano carbons and structural deformation took place consecutively. Based on the FFT analysis, we can rationalize the critical role of nucleation in the carburization of the iron nanoparticle in presence of syngas, which hasn't been discusses in reference. This work not only successfully performs the real-time high spatial resolution characterizations of the dynamic FTS albeit under low pressure conditions, but also sheds new light into the surface reconstruction of iron nanoparticles correlated with the carburization process promoted by syngas. Therefore, the nucleation-dominated process suggests a complementary model related with catalysts activation. Theoretical model of the activated iron surface can be proposed on the base of the in situ characterizations with high-spatial resolutions, which will improve our mechanical understanding about FTS.

## References

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