

In situ TEM-EELS activation of iron Fischer-Tropsch catalysts

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Introduction

“Fischer-Tropsch synthesis” is a catalytic conversion of synthesis gas to a high quality synthetic petroleum substitute. The simplified reaction is: $n \text{ CO} + (2n + 1) \text{ H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + n \text{ H}_2\text{O}$. During this process iron carbides are formed that are believed to be the active species. An accepted model that describes the activation is the so called shell-core model [1]. This model suggests that upon contact with syngas, lattice oxygen atoms at the Fe_2O_3 surface are removed by reaction with H_2 or CO (producing H_2O or CO_2 respectively). This leads to a different iron-oxide: Fe_3O_4 . The Fe_3O_4 is then converted to iron carbides (FeC_x). The activation is generally performed in situ inside the catalytic reactor. Once activated, the catalyst is sensitive to air [2]. The best catalytic performance is often obtained for iron oxide precursors activated using carbon monoxide. Studying the activation process is not unambiguous. Using in situ TEM-EELS measurements using an environmental cell enabled us to follow the evolution of specific nanoscale areas while mimicking the activation procedure; viz. by flowing CO gas inside the microscope at elevated temperatures. By using a combination of TEM and EELS, we found that the activation mechanism is different compared to data published so far.

Materials and Methods

Samples for in situ synthesis were prepared by dispersing a catalyst precursor onto 50 mesh pure Pt (99.997%) grids. The catalyst precursor consisted of iron oxide and potassium carbonate. In situ synthesis of the nanoparticles was performed in a Tecnai F-20 field emission ETEM operating at 200 kV. The ETEM is equipped with a Gatan Imaging Filter; thus electron energy-loss spectroscopy can be employed. In situ high-resolution electron microscope (HREM) images were recorded with a Gatan CCD camera using DigitalMicrograph 3.1TM software. The catalyst samples were mounted into a Gatan Inconel heating holder.

Results and Discussion

TEM revealed that the catalyst precursor contained iron oxide crystallites up to 30 nm in size, as shown in Figure 1a. This Figure shows our catalyst at the start of our experiments in 1 Torr of N_2 at 150°C (reaction time = 0 minutes). The catalyst activation procedure was mimicked by increasing the temperature to 270°C and increasing the CO pressure was. Due to the limitations of the environmental cell, a maximum pressure of 20 Torr was applied. Our results show that, in the first stage of this activation process, Fe_2O_3 is reduced to Fe_3O_4 . During this reduction, severe sintering takes place (compare Figures 1a and b).

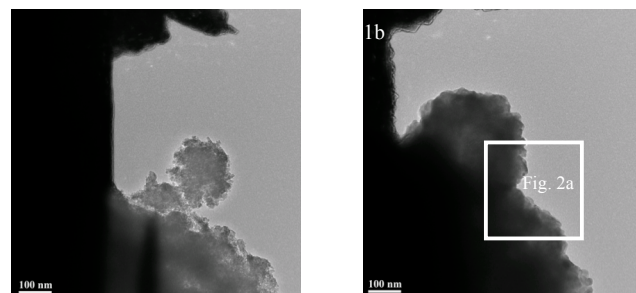


Figure 1 a-b: TEM images of the same area before (a, time = 0 min) and after sintering (b; time = 350 min)

After 600 minutes reaction time, new features appeared on the surface of the sintered iron oxide particles (see Figure 2a). EELS proves these features are iron carbides (Figure 2b).

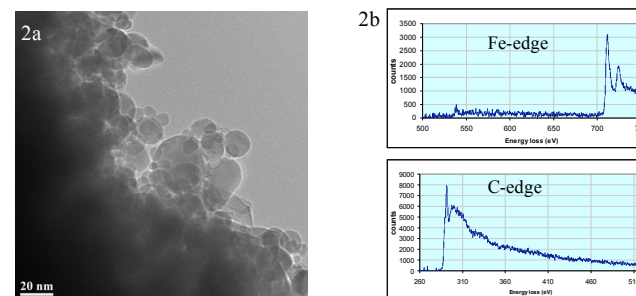


Figure 2 a-b: TEM (a) and EELS data (b) showing iron carbide formation after 600 minutes. The TEM area shown is a magnification of the area indicated in Figure 1b.

Interestingly, EELS data show metallic iron is an intermediate in the formation of the iron carbides (not shown). Overall, the activation mechanism is different compared to the shell-core model. During the presentation, we will show more examples and elaborate on the new activation mechanism.

Significance

Since syngas can, amongst other resources, be derived from biomass, the Fischer-Tropsch process is likely to become one of the key technologies to produce sustainable transportation fuels.

References

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