Fuelling nature to pr

Transportation fuels that reduce emissions are a promising answer to our polluted world. Despite its discovery in the 1920s, Fischer-Tropsch catalysis may well be a good candidate for a cleaner future. Colourless, odourless and low in toxicity, Fischer-Tropsch-based diesel fuel reduces sulphur, nitrogen oxide and carbon dioxide emissions compared with regular diesel, and it does not require engine modifications in vehicles for its use.

Image of the gas to liquids (GTL) plant of Shell in Malaysia. GTL is a refinery process to convert natural gas or ot

Hydrocarbons, such as crude oils, bitumen and natural gas, are still available in nature, so Fischer-Tropsch (FT) synthesis has only been partially popular since its discovery back in 1925. In certain moments in history it became relevant when there was a lack of easily available crude oil: during World War II its use was mostly military, later, the oil crisis in the 1970s led to some recovery of interest in FT. Today, the fact that natural liquid hydrocarbons are becoming less abundant, not easily accessible and containing more impurities, such as sulphur, nitrogen and metals, and that there is an increasing pressure for a more sustainable society, has put FT back in the limelight.

FT technology converts natural gas, coal or biomass to clean-burning fuel or hydrocarbons. In a first step, these resources are converted to synthesis gas, in short syngas (mixtures of carbon monoxide and hydrogen). Then the syngas reacts on a cobalt or iron catalyst to yield hydrocarbons in a kind of polymerisation process, leading to mainly long-chain hydrocarbons or waxes. These are often broken up again in diesel fuel molecules.

Cobalt catalysts are considered the most effective for the synthesis of long-chain hydrocarbons. These catalysts are optimised for conversion of stochiometric syngas mixtures, mainly coming from natural gas. On the other hand, iron-based FT catalysts are normally used for the conversion of synthesis gas from coal and they are promising catalysts for the conversion of biomass because they possess water–gas shift properties (i.e. altering the hydrogen to carbon monoxide ratio in synthesis gas). At the ESRF, users study both types of catalysts.

Scientists are trying to find out what happens during the FT reaction and with this knowledge they want to design more active and stable catalyst materials. The deactivation of a FT catalyst results in a gradual decrease in the FT reaction rate. There are many possible reasons for FT deactivation, such as reoxidation of active sites, sintering, catalyst poisoning from impurities in the syngas feed, polymeric surface carbon formation or surface metal-support compound formation (Tsakoumis *et al.* 2010). FT catalysts operate in multiphase medium and at higher pressures and temperatures. Not so long ago, the only way to study these catalyst systems was through *ex situ* methods of catalyst characterisation. These are not reliable due to the changes that the structure can undergo when withdrawn from the reactor. For example, cobalt metal particles can be reoxidised when exposed to air.

Using synchrotron methods and with a proper sample environment where the reaction conditions can be reproduced (i.e. high temperature, syngas reaction environment and preferably high pressures), scientists can now perform a direct *in situ* or *in operando* characterisation of a catalyst in FT reactions. The wide array of techniques allows scientists to get information on different aspects of catalysis structure, such as the nature of crystalline phases, sizes of metal and oxide nanoparticles (X-ray diffraction) or the oxidation state of the atoms surrounding the catalyst (X-ray absorption fine structure spectroscopy or XAFS). Where possible, these synchrotron-based techniques are directly combined with more conventional methods, such as Raman spectroscopy.

At the Swiss Norwegian Beamline (SNBL – BM1), scientists have tested cobalt catalysts over several years. The team at SNBL has built

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her gaseous hydrocarbons into liquid synthetic fuels, using a syngas as an intermediate in FT.

a set-up with an *in situ* cell in collaboration with the Norwegian University of Science and Technology (NTNU) in Trondheim. In the cell, they include a small catalyst and a reaction mixture and observe the state of the catalyst under industrial conditions. According to Olga Safonova, scientist at BM1: "This sample environment allows the reproduction of experimental conditions (high pressure up to 20 bar, high temperature, space velocity of syngas and FT reaction rates) close to the ones used in industry. The set-up is suitable to perform structural studies on working FT catalysts using X-ray diffraction, X-ray absorption spectroscopy and Raman spectroscopy."

A team from the University of Lille recently carried out experiments on an alumina-supported cobalt catalyst using X-ray diffraction. The results showed that at a pressure of 20 bar and a temperature of 220 °C, i.e. industrially relevant conditions, cobalt sintering took place during three to five hours of reaction. After eight hours of experiment, the cobalt in some catalysts would, to a smaller extent, transform into cobalt carbide. These two processes contributed to the deactivation of FT catalysts (Karaca *et al.* 2010).

In similar conditions, the team from the Norwegian University of Science and Technology carried out experiments using X-ray diffraction and X-ray absorption near edge structure (XANES) to reveal information about cobalt-based FT catalyst promoted with rhenium. Small amounts of noble metals like rhenium are added to FT synthesis in order to improve it. In the case of rhenium, it increases dispersion of the catalyst. This time the scientists studied the changes in the cobalt crystallites during FT synthesis in two different conditions: first, at FT synthesis conditions (483 K, 18 bar and low gas hourly space velocity) no significant changes in the cobalt crystallites were observed during the first hours of reaction. Cobalt carbide was not formed in these conditions. Running the reaction at higher temperatures and predominantly methanation conditions led to significant sintering of the cobalt particles and a further reduction of a partially reduced catalyst. This demonstrates how sensitive this complex reaction is to the reaction conditions (Rønning *et al.* 2009).

Iron-based catalysts have similar mechanisms to the cobalt ones. They consist of a precipitated iron oxide phase to which elements are added to improve the catalytic process. Scientists from the University of Utrecht (the Netherlands) went to the DUBBLE beamline (BM26) to measure the reaction process in different iron-based FT systems, including different amounts of additives. Typical so-called promoters are copper, potassium and silicon dioxide. The latter is added to disperse iron phases and to prevent sintering and attrition of the active catalyst, copper improves the reducibility of the catalyst and potassium is used to improve the selectivity of the catalyst towards longer hydrocarbon chains. The team combined XAFS and wide-angle X-ray scattering (WAXS) techniques to get complementary information. WAXS showed crystalline phases to be present after activation and during FT synthesis, and XAFS analysis suggested that, for some catalysts, the majority of iron was present in amorphous phases, which were harder to detect by WAXS (de Smit *et al.* 2009).

Industrial use

This type of research might seem very fundamental, but FT technology is already being used in several pilot and large commercial refineries all over the world (South Africa, Malaysia, Qatar, China) and most of the work done at the ESRF is somehow linked to industrial uses: companies like Shell, Total or Statoil often appear in the scientific results. The probable worldwide leader in FT research, though, is Sasol, a South African company that has been producing fuel this way since 1950. Sasol has made the most of the coal mines in South Africa and it extracts nearly 50 million tons of coal annually.

Researchers from SASOL have already visited ID31 twice trying to find the structure of a carbide generally considered responsible for the FT activity in iron-based FT systems. The second time, they brought with them a reaction chamber at 20 bar that could reach up to 300 °C, in order to reproduce the exact conditions in industry.

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