



In situ and *operando* structural characterisation of a Fischer–Tropsch supported cobalt catalyst

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ABSTRACT

In order to improve cycle length, catalytic activity and selectivity towards heavy paraffins of Fischer–Tropsch cobalt-based catalysts a better comprehension of the structure and behaviour of supported nano-sized metallic cobalt in Fischer–Tropsch synthesis is meaningful.

A new X-ray absorption cell dedicated to *in situ* and *operando* experiments in heterogeneous catalysis has been built and tested on the SAMBA beamline at SOLEIL. Thanks to new equipments implemented on the SAMBA beamline (Quick-EXAFS monochromator, gas distribution system. . .), we are now able to solve local structure of Fischer–Tropsch catalysts under realistic working conditions and improve our knowledge of catalytic property-structure relationship. The efficiency of this setup is illustrated by an *operando* study of a cobalt-supported catalyst.

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1. Introduction

The Fischer–Tropsch (FT) process is one of the most promising processes to produce clean liquid fuels from syngas (mixture of carbon monoxide and hydrogen). It allows rational utilization of fossil and renewable resources (natural gas, coal and biomass). The energy crisis, the growing demand for cleaner fuels and a more rational utilization of resources (coal, natural gas, biomass. . .) have largely contributed to a major revival of FT synthesis in the recent past.

Cobalt-supported catalysts are a system of choice for the low temperature FT synthesis [1]. The reaction typically proceeds at 210–250 °C, with a total pressure of 20–30 bar and a H₂/CO ratio close to 2.

It is generally accepted that the active sites for FT synthesis over cobalt-based catalysts are metallic cobalt surface sites. Their catalytic properties depend directly on the number and availability of these active sites [1]. Before activation the cobalt is present as a Co₃O₄ spinel phase. Depending on the reduction treatment (temperature, nature of gas. . .), the activation step leads to the formation of different metallic cobalt particles (cubic or hexagonal structures, presence of stacking faults) dispersed on the oxide support [2]. Moreover water produced during catalyst reduction may result in non-reducible cobalt aluminates formation [3].

During FT synthesis, structural changes may result, for example, in a significant decrease in the number of the active sites inducing a lowering of the activity and selectivity. That is why a better comprehension of the behaviour of supported nano-sized metallic cobalt is meaningful in order to improve cycle length and catalytic properties of FT catalysts. The high air sensitivity of FT catalysts and the presence of hard wax on used catalysts limit considerably the choice of relevant characterisation techniques. Because of the lack of direct characterisation of cobalt-based catalysts in realistic working conditions, information about changes appearing during the activation and deactivation steps is rather contradictory. Numerous deactivation mechanisms, recently reviewed [4,5] are proposed in the literature: poisoning, sintering, surface carbon formation, carburization, cobalt re oxidation, cobalt-support mixed compounds formation, surface reconstruction and attrition. Moreover reaction conditions such as temperature, pressure, conversion, partial pressures of syngas, products (water, oxygenates. . .) and the type of reactor (fixed bed or slurry bubble column reactor) are sensitive points to understand the FT catalyst deactivation. Hence the characterisation of the evolution of catalysts structure during FT reaction still represents a significant challenge because of harsh reaction conditions (high temperature, high pressure. . .).

X-ray Absorption Spectroscopy (XAS) provides powerful structural and chemical information about a selected element in a material. A particular strength of this technique is that the penetrating nature of the X-rays makes possible studies of materials under the conditions of their use, including high temperatures, pressures and reactive atmospheres. Thus, XAS is a powerful method

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for local order characterisation of catalysts under working conditions. Thanks to new equipments and using time-resolved coupled *operando* structural analysis, it is now possible to greatly improve our knowledge on catalytic property-structure relationship [6].

The possibility of performing time, temperature and pressure-resolved experiments has led to the design of different *in situ* cells that mimic conditions close to the catalytic reaction conditions. In order to correlate structural and catalytic properties, the working conditions in the *in situ* XAS cell have to be similar to those usually met in catalytic reactors [7]. Thus temperature, pressure and flow properties have to be precisely controlled as in catalytic reactors. In most conventional reactors used for catalytic tests in industrial plants, the catalyst is present as a dispersed powder. Thus to be more representative of realistic phenomena, studies should be performed in the same testing conditions by using a fixed bed reactor loaded with a powdery sample.

Three designs were originally published in literature: those initially developed by Lytle et al. [8], Kammers et al. [9], Clausen and Topsøe [10]. Subsequently, various reactive cells have been developed [11–19]. Among them, there are two general categories: those that are a plug-flow reactor based on powdery samples ideal for mimicking catalytic reactions and those that are a packed bed reactor using pellets optimized for X-ray absorption spectroscopy at the detriment of the catalytic performances. Actually it is often difficult both to optimize the absorption data quality and to obtain homogeneity of the sample temperature under dynamic conditions. Additionally when dealing with high pressure reactions, only few XAS cells, with a “real” catalytic fixed bed was described in the literature. Recently Kawai et al. [20] developed a new XAS cell for high pressure analysis. This cell has inspired us for the design of the catalytic cell presented in this paper with some improvements regarding the cost and versatility of use. A key development for the work described here, is the construction of a low-volume cell with flat X-rays transparent windows that are chemically, structurally, and thermally stable. The performances of the new X-ray absorption cell will be evaluated with a Quick-EXAFS (QEXAFS) study of the local order of cobalt atoms in a supported Fischer–Tropsch catalyst.

2. Experimental

2.1. Catalyst preparation

A cobalt-based model catalyst was prepared via incipient wetness impregnation over an alumina-based carrier (BET surface area = $171 \text{ m}^2 \text{ g}^{-1}$, pore volume = 0.52 mL g^{-1} and 10 nm average pore size calculated from BJH nitrogen desorption branch) using an aqueous solution of cobalt nitrate (Sigma–Aldrich, 99.999% purity), to achieve a cobalt loading of 7 wt.%. Subsequently, the impregnated catalyst was dried by direct heating of the sample from room temperature (RT) to 120°C for 2 h. Then the catalyst was calcinated at 400°C under dry air and finally activated by a reduction treatment under pure hydrogen.

2.2. Catalyst characterisation

The as-prepared catalyst was characterised by X-Ray Diffraction (XRD) for phase identification and average crystallite size determination. XRD patterns were recorded at room temperature by a PANalytical X'Pert Pro diffractometer using the $\text{Cu K}\alpha$ radiation.

The reducibility of the catalysts was studied by Temperature Programmed Reduction (TPR) analysis obtained by passing a 5% H_2/Ar gas mixture through the catalyst while increasing the temperature at a constant rate ($10^\circ\text{C}/\text{min}$).

With a new *in situ* cell for X-ray Absorption Spectroscopy (XAS) implemented on the SAMBA beamline at SOLEIL (Source Optimisée

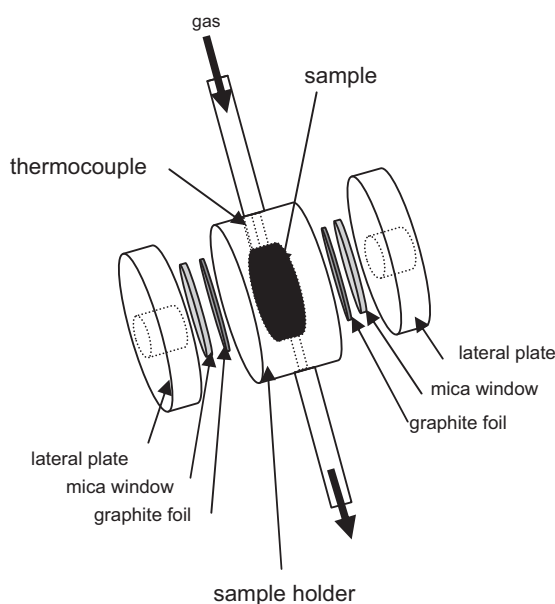


Fig. 1. Schematic drawing of the main parts of the cell.

de Lumière d'Énergie Intermédiaire du LURE, Saint-Aubin, France) operating in its time-resolved operation mode available with its Quick-EXAFS monochromator [21], one can observe structural changes at realistic working conditions of FT reaction (temperature, pressure. . .) with a time resolution of one second.

2.3. XAS measurements

2.3.1. Design of the new X-ray absorption cell

A new X-ray absorption cell dedicated to *in situ* and *operando* experiments in heterogeneous catalysis has been built for this work [22]. The XAS cell can be used with a powder sample or a pellet under high temperature (600°C), high pressure (50 bar) and under the flow of a large number of oxidizing or reducing gas mixtures. This new micro-reactor is displayed in Figs. 1 and 2.

The body of the cell, made of stainless steel, consists of three main parts: the sample holder with a gas circulation system (as the central part of the cell) and two lateral plates (Fig. 1). Lateral and central parts are assembled and sealed using graphite foils. The

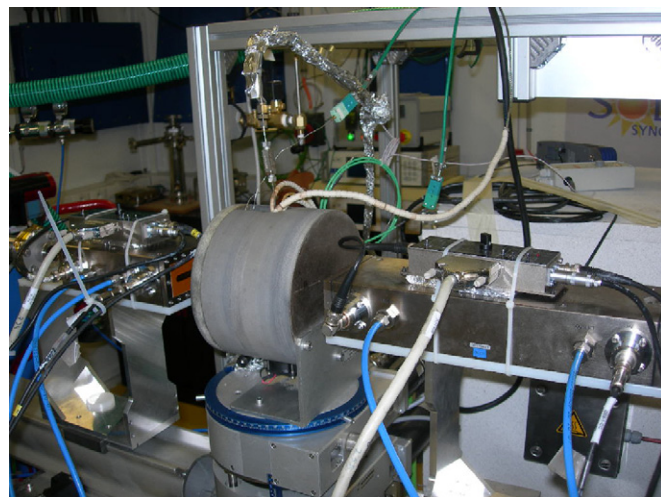


Fig. 2. Photograph of the fully assembled system at the SAMBA beamline ready for experiment.

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