Catalysis Today 171 (2011) 186–191

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

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

Amélie Rochet[a,b], Virginie Moizan[a,*], Christophe Pichon[a], Fabrice Diehl[a], Adrien Berliet[a], Valérie Briois[b]

[a] *IFP Energies nouvelles, Etablissement de Lyon, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France*
[b] *Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France*

ARTICLE INFO

Article history:
Received 29 October 2010
Received in revised form 11 March 2011
Accepted 29 March 2011
Available online 1 June 2011

Keywords:
Operando
In situ XAS cell
QEXAFS
Cobalt-supported catalyst

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.

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 H_2/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 Co_3O_4 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, carbidization, 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

* Corresponding author. Tel.: +33 4 37 70 23 59.
E-mail address: virginie.moizan@ifpen.fr (V. Moizan).

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2011.03.079

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 lead 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], Kampers 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 $m^2\,g^{-1}$, 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 Cu Kα 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 °C/min).

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

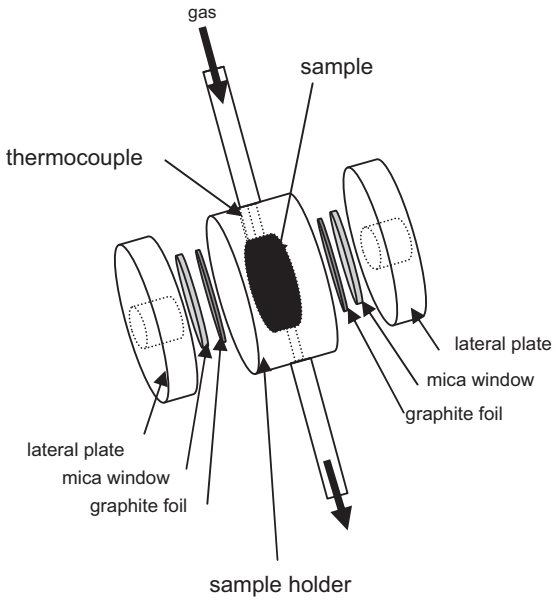

Fig. 1. Schematic drawing of the main parts of the cell.

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

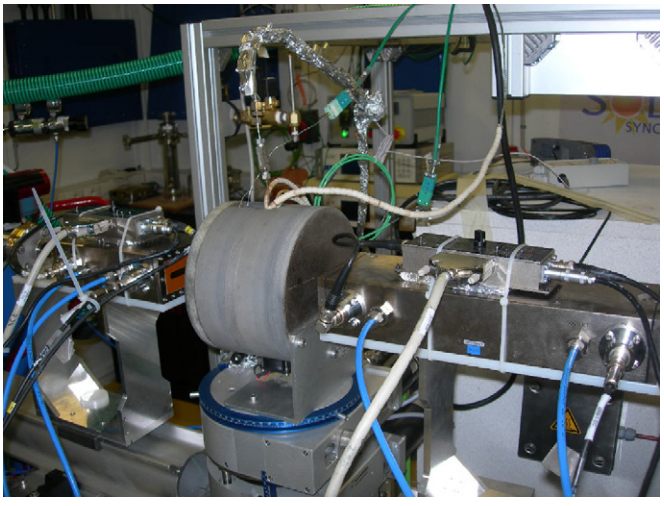

Fig. 2. Photograph of the fully assembled system at the SAMBA beamline ready for experiment.

lateral parts retain the windows by pushing them strongly against the central body.

The sample holder is the central part. It is made of a cavity of volume equal to 0.35 mL filled by the catalyst. Due to cavity's dimension (diameter = 13 mm), it is easy to work either with a standard pellet of catalyst or with sample made of compacted powder.

In this setup, the choice of proper windows material is sensitive and essential. Actually, the X-ray transparent windows maintain the catalyst powder in the sample holder, let X-rays go through the cell and withstand harsh reaction conditions (high pressures, high temperatures and reactive gas flow). We selected 25 μm thick mica windows. This material presents good mechanical properties, a good transmittance for X-rays above 7 keV (Co K-edge region), a low cost and a negligible gas permeability.

A heating ceramic band placed around the cell can homogeneously heat the catalyst from RT to 600 °C. In order to control precisely the sample temperature, a thermocouple is placed closely to the catalyst sample in a hole drilled into the cell body. A programmable temperature controller operates the *in situ* cell.

The gas flow rates are precisely controlled with a gas distribution system developed on the SAMBA beamline. At the reaction cell outlet, an on-line gas analysis equipment like a mass spectrometer can be used to measure catalytic properties of the sample.

2.3.2. XAS measurements

XAS measurements were carried out with the Quick-EXAFS (QEXAFS) monochromator available on the SAMBA beamline at SOLEIL [21]. XAS spectra were measured in transmission mode with OKEN ionization chambers as X-rays detectors.

The Si(1 1 1) channel-cut crystal was tuned to a Bragg angle of 13.9°. An amplitude of 2.2° crystal oscillation around this value was chosen to acquire an entire EXAFS spectrum at the Co K-edge. An oscillation frequency of 1 Hz was used for the crystal movement to obtain each second two spectra of 4800 points with an average energy step of 0.25 eV and an integration time of 104 μs per each point. This oscillation frequency was sufficient to get an adequate time resolution for the studied reactions.

2.3.3. XAS data analysis

Analysis of the XAS data was performed by using the Athena graphical interface program [23]. Ten subsequent spectra were merged to improve the signal-to-noise ratio. Then the spectra were normalized using the flattening algorithm in the default energy range used by Athena.

The identification of the cobalt phases present during *in situ* treatment was done by linear combination of the spectra (from −80 to 100 eV around the edge). Spectra from the freshly calcined catalyst were used as reference for Co_3O_4. A commercial CoO, a cobalt aluminate and a cobalt foil were used as references.

2.3.4. In situ treatment

During the activation treatment, the catalyst was exposed to a pure hydrogen flow of 20 mL/min at atmospheric pressure. The temperature is increasing from RT to 400 °C with a 5 °C/min heating rate.

After reduction, the temperature was decreased to 250 °C under hydrogen flow before pressuring the reactor up to 18 bar. When this pressure was reached, the synthesis gas with a H_2/CO ratio equal to 2 was then introduced.

2.4. In situ XAS cell as a micro-reactor

Prior to use the new X-ray absorption cell at the synchrotron radiation facility it was tested as an independent catalytic microreactor on Fischer–Tropsch catalytic micro unit available in the catalysis laboratory at IFP Energies Nouvelles. The reactor was connected to a gas chromatograph to analyse on-line the gaseous products (carbon atom number under around ten/eleven). To prevent condensation of liquid products the gas lines were heated up to 150 °C. Catalytic properties obtained with the cell are presented in Fig. 3. The aim was to check that the performance observed with the X-ray absorption cell was similar to those obtained with catalytic test units conventionally used at IFP Energies Nouvelles.

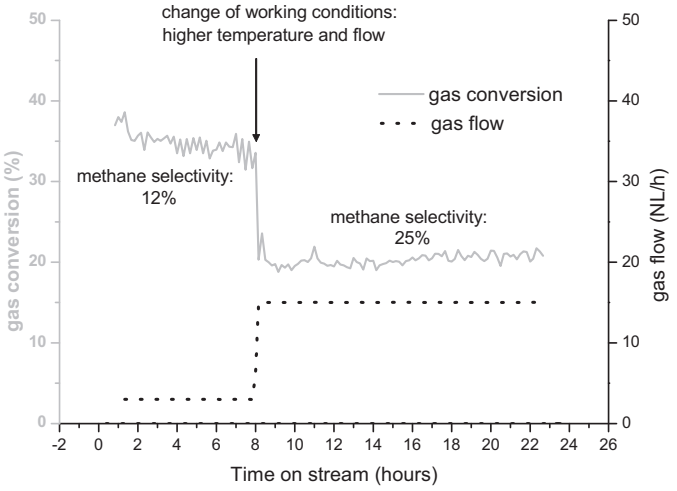

Fig. 3. Catalytic properties of the catalyst placed in the XAS cell.

After activation under pure hydrogen, the catalyst was placed under syngas with a H_2/CO ratio equal to 2. To check the catalytic behaviour of our sample loaded in the XAS cell, we chose to work with two temperatures conditions. Due to a too weak gas conversion at 230 °C (standard temperature for the Fischer–Tropsch process) and to avoid the plug of the exhaust capillary with high products the catalytic tests were conducted at 250 °C and 280 °C. The sample was maintained at 250 °C for the first hours then the catalyst was heated up to 280 °C and the syngas flow was increased.

During the first hours at 250 °C and 20 bar, no visible changes of catalytic properties were observed. The cobalt catalyst exhibited at a gas-space velocity of about 2.4×10^{-3} s^{-1}, around 12% methane selectivity at 35% carbon monoxide conversion.

It is only after increasing the temperature up to 280 °C and the gas flow that we observed a change in gas conversion (Fig. 3). At 280 °C with a gas-space velocity of 1.2×10^{-3} s^{-1} the gas conversion is much lower (20%) than the conversion at 250 °C and methane selectivity is increased up to 25%.

3. Results and discussion

This work focuses on studying the structure of a model 7 wt.% cobalt loading catalyst supported on alumina-based carrier in industrially relevant Fischer–Tropsch reaction conditions. The freshly calcined catalyst is composed of Co_3O_4 as observed on Fig. 4 with XRD. The average crystallite size of Co_3O_4 was calculated according to the Scherrer formula [24] using the (3 1 1) peak at $2\theta = 36.8°(2\theta)$ after subtracting the signal of the support. The average size of cobalt particles after calcination is 14 nm (±10%).

Fig. 5 shows the TPR profile of the cobalt catalyst supported by alumina-based carrier. The profiles exhibit three groups of hydrogen consumption peaks: low, medium and high temperature peaks. The low temperature peak can be attributed to the reduction of Co_3O_4 to CoO. The second large peak is mainly attributed to the reduction of CoO particles and cobalt oxides interacting more strongly with the support. The last one, at higher temperature (900 °C), is probably due to the reduction of cobalt aluminates type compounds.

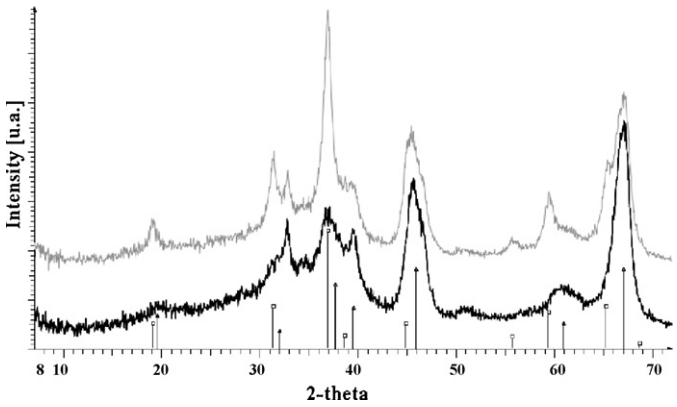

Fig. 4. XRD patterns of calcined catalyst (grey) and alumina-based support (black) (□ Co_3O_4, ▲ alumina).

Quick-XANES spectra were recorded during the entire reaction: first during the reduction treatment (under pure hydrogen at atmospheric pressure) and then during the Fischer–Tropsch reaction under syngas at high pressure. With XANES profiles, it is possible to observe changes in cobalt oxidation states. Some X-ray absorption spectra collected during the activation treatment under pure hydrogen of the powdery catalyst are plotted in Figs. 7 and 8. Time resolved investigation of the structural and electronic changes with a time scale of 100 s – which corresponds to a temperature window of 8 °C – is reported with a 3D plot in Fig. 8.

During the heating ramp, we clearly observe a shift at lower energies of the rising edge with an increase of its intensity. This feature is consistent with a reduction of the cobalt oxide phase of the catalyst. The Co_3O_4 spinel structure is transformed in CoO. Then we observe a decrease of intensity of our signal. It corresponds to the reduction into Co^0. This two steps reduction confirms results obtained with TPR profiles and are in agreement with those obtained in other *in situ* studies [25,26].

At the end of the reduction treatment the cobalt phase is not completely reduced to metallic cobalt. Thanks to linear combination fits of the spectra recorded during the activation using of the spectra of relevant reference compounds (Fig. 6), we can evaluate the reduction rate of our catalyst. Thus the catalyst was only partially reduced after treatment in hydrogen at 400 °C. About 40% of cobalt is in a metallic phase and 60% is still present as CoO at the end of the activation treatment (Fig. 9).

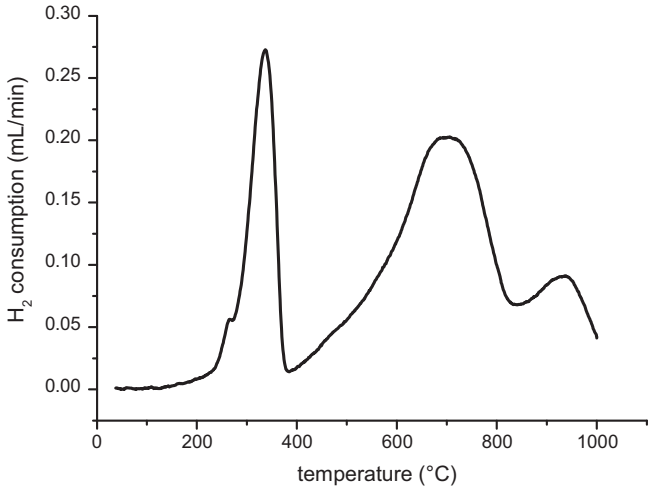

Fig. 5. TPR profiles of the calcined catalyst prepared with 7 wt.% cobalt loading.

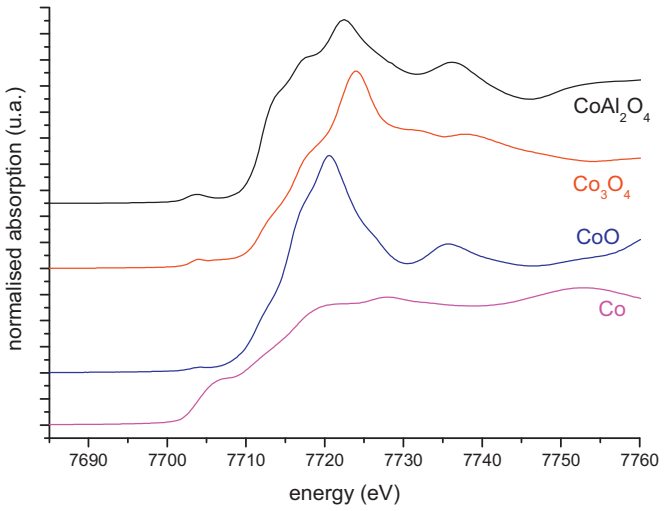

Fig. 6. XANES spectra of references compounds.

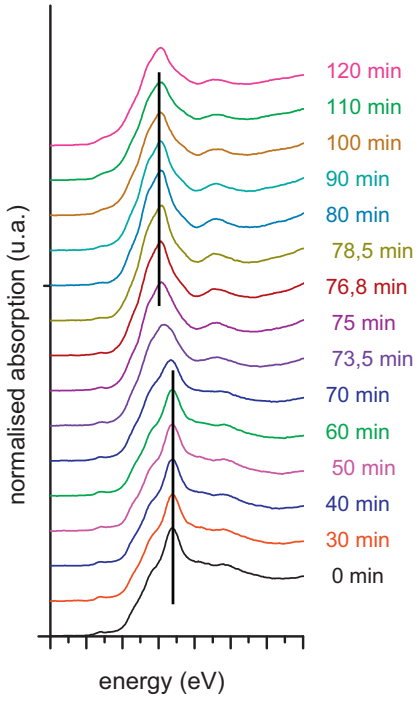

Fig. 7. XANES profiles during reduction of the catalyst in the XAS cell.

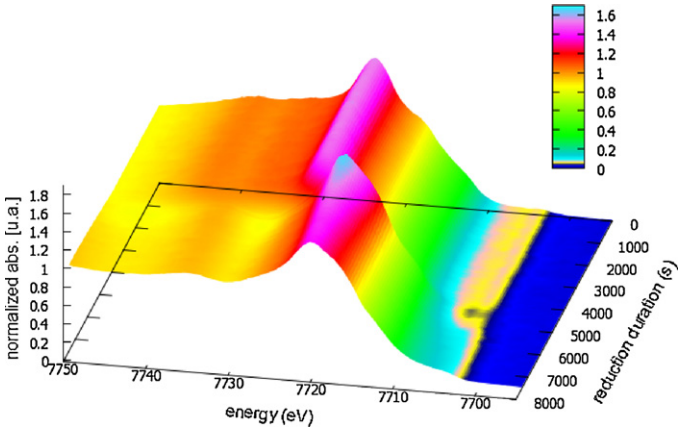

Fig. 8. Some XANES spectra collected during the activation of the catalyst in the XAS cell.

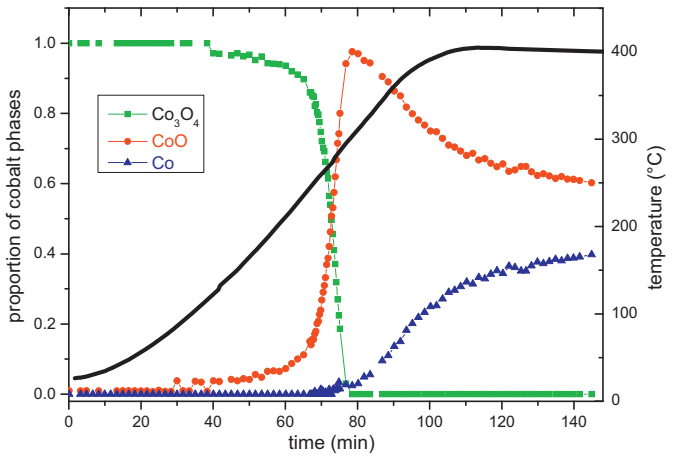

Fig. 9. Phases compositions obtained by linear combination fits during the activation of the catalyst in the XAS cell. The solid line shows the temperature profile.

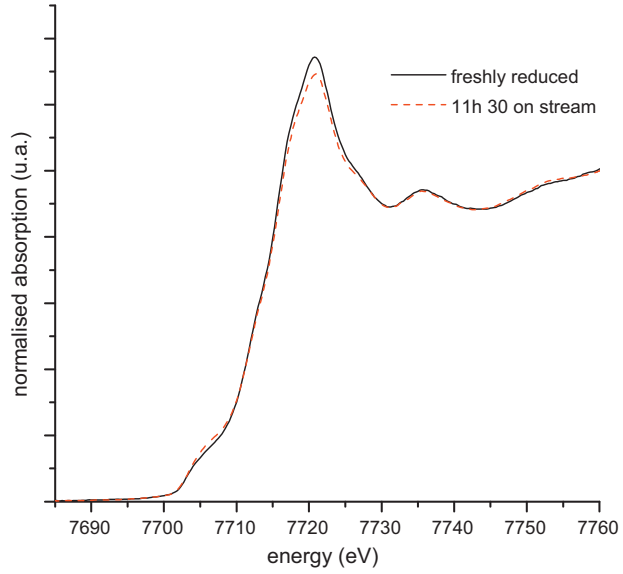

Fig. 10. XANES spectra collected during the Fischer–Tropsch reaction of the catalyst in the XAS cell.

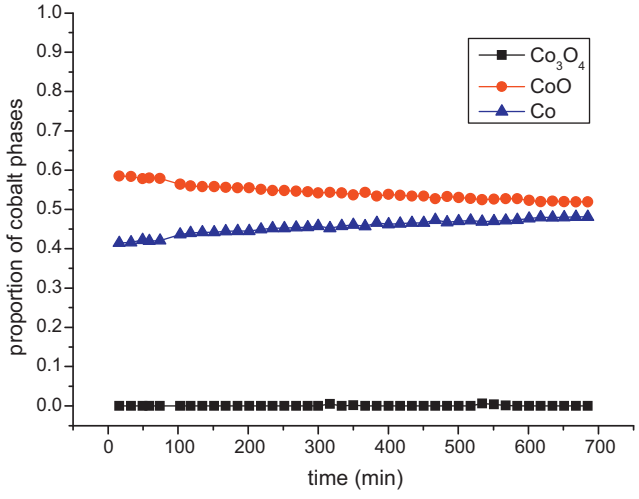

Fig. 11. Phases compositions obtained by linear combination fits during the Fischer–Tropsch reaction of the catalyst in the XAS cell.

Quick-XANES were also recorded during the Fischer–Tropsch synthesis under pressure of syngas at 250 °C during about 12 hours (Fig. 10).

No very important changes in the XANES spectra were detected during the first hours under syngas. Results of linear combinations fits are presented on Fig. 11. Contrary to some deactivation mechanisms proposed in literature [4,5] no cobalt oxidation was observed with partially reduced cobalt species under realistic conditions of Fischer–Tropsch synthesis. We observe a slight further reduction of the cobalt catalyst after about 12 h under syngas. Thus under realistic working conditions of Fischer–Tropsch reaction the cobalt catalyst seems to carry on its reduction. These results are also consistent with previous *ex situ* characterisation studies [27,28] and with more recent *in situ* XRD studies [29,30].

4. Conclusions

A new *in situ* X-ray Absorption Spectroscopy cell dedicated to reactions at high pressure was successfully used for Quick-EXAFS studies of a cobalt supported Fischer–Tropsch catalyst under realistic working conditions (activation under pure hydrogen at 400 °C and reaction at 250 °C, under 18 bar of syngas). This cell represents a real catalytic fixed bed reactor able to mimic harsh reaction conditions. It can be used over a wide process variable range, at different X-ray energies and for a wide array of heterogeneous catalysts.

A 7 wt.% cobalt loading catalyst supported on alumina-based carrier has been characterised in a QEXAFS study under realistic working Fischer–Tropsch conditions (250 °C, 18 bar). A slight further reduction of the catalyst was observed during the first hours under syngas.

A study of the Fischer–Tropsch reaction under realistic working conditions extending beyond the first hours will be necessary to give further information about the causes of catalysts deactivation in the Fischer–Tropsch process.

Acknowledgements

The authors would like to thank Bernard Langlois for his advice and assistance in the *in situ* cell design. The authors would like also to acknowledge Laurent Barthe and Laurent Lemaitre for their technical assistance and Florian Meneau for helpful discussions. The authors are grateful to SOLEIL committees for beam time allocated on the SAMBA beamline.

References

[1] A.Y. Khodakov, Catal. Today 144 (2009) 251.
[2] O. Ducreux, B. Rebours, J. Lynch, M. Roy-Auberger, D. Bazin, Oil Gas Sci. Technol. (2009) 1.
[3] A. Sirijaruphan, A. Horvath, J.G. Goodwin, R. Oukaci, Catal. Lett. 91 (2003) 89.
[4] A.M. Saib, D.J. Moodley, I.M. Ciobîca, M.M. Hauman, B.H. Sigwebela, C.J. Weststrate, J.W. Niemantsverdriet, J. van de Loosdrecht, Catal. Today 154 (2010) 271.
[5] N.E. Tsakoumis, M. Rønning, Ø. Borg, E. Rytter, A. Holmen, Catal. Today 154 (2010) 162.
[6] C. La Fontaine, L. Barthe, F. Villain, V. Briois, F. Baudelet, Q. Kong, X. Secordel, A. Yoboué, E. Berrier, S. Cristol, P. Massiani, E. Marceau, X. Carrier, XAFS 14 Conference, Camerino, 2009.
[7] J.D. Grunwaldt, M. Caravati, S. Hannemann, A. Baiker, Phys. Chem. Chem. Phys. 6 (2004) 3037.
[8] F.W. Lytle, R.B. Greegor, E.C. Marques, D.R. Sandstrom, G.H. Via, J.H. Sinfelt, J. Catal. 95 (1985) 546.
[9] F.W.H. Kampers, T.M.J. Maas, J. van Grondelle, P. Brinkgreve, D.C. Koningsberger, Rev. Sci. Instrum. 60 (1989) 2365.
[10] B.S. Clausen, H. Topsøe, Catal. Today 9 (1991) 189.
[11] S.R. Bare, N. Yang, S.D. Kelly, G.E. Mickelson, F.S. Modica, Catal. Today 126 (2007) 18.
[12] D.G. Barton, S.L. Soled, G.D. Meitzner, G.A. Fuentes, E. Iglesia, J. Catal. 181 (1999) 57.
[13] C. Geantet, Y. Soldo, C. Glasson, N. Matsubayashi, M. Lacroix, O. Proux, O. Ulrich, J.L. Hazemann, Catal. Lett. 73 (2001) 95.

[14] J.S. Girardon, A.Y. Khodakov, M. Capron, S. Cristol, C. Dujardin, F. Dhainaut, S. Nikitenko, F. Meneau, W. Bras, E. Payen, J. Synchrotron Radiat. 12 (2005) 680.
[15] S. Hannemann, M. Casapu, J.D. Grunwaldt, P. Haider, P. Trussel, A. Baiker, E. Welter, J. Synchrotron Radiat. 14 (2007) 345.
[16] H. Huwe, M. Froba, J. Synchrotron Radiat. 11 (2004) 363.
[17] G. Meitzner, S.R. Bare, D. Parker, H. Woo, D.A. Fischer, Rev. Sci. Instrum. 69 (1998) 2618.
[18] M.S. Nashner, A.I. Frenkel, D.L. Adler, J.R. Shapley, R.G. Nuzzo, J. Am. Chem. Soc. 119 (1997) 7760.
[19] R. Revel, D. Bazin, A. Seigneurin, P. Barthe, J.M. Dubuisson, T. Decamps, H. Sonneville, J.J. Poher, F. Maire, P. Lefrancois, Nucl. Instrum. Methods Phys. Res., Sect. B 155 (1999) 183.
[20] T. Kawai, W.J. Chun, K. Asakura, Y. Koike, M. Nomura, K.K. Bando, S.T. Oyama, H. Sumiya, Rev. Sci. Instrum. 79 (2008) 014101.
[21] V. Briois, E. Fonda, S. Belin, L. Barthe, J.V. Lauritsen, F. Langlois, M. Ribbens, F. Villain, UVX 2010, 2009.
[22] A. Rochet, V. Moizan, V. Briois, C. Pichon, 7th International Conference on Synchrotron Radiation in Materials Science, Oxford, 11–14 July 2010, 2010.
[23] B. Ravel, M. Newville, J. Synchrotron Radiat. 12 (2005) 537.
[24] B.D. Cullity, Elements of X-ray Diffraction, Addision-Wesley, London, 1978.
[25] A.Y. Khodakov, J. Lynch, D. Bazin, B. Rebours, N. Zanier, B. Moisson, P. Chaumette, J. Catal. 168 (1997) 16.
[26] M. Sadeqzadeh, H. Karaca, O.V. Safanova, P. Fongarland, S. Chambrey, P. Roussel, A. Griboval-Constant, M. Lacroix, D. Curulla-Ferré, F. Luck and A.Y. Khodakov, Catal. Today 164 (2011) 62, this issue.
[27] A.M. Saib, A. Borgna, J.V. de Loosdrecht, P.J. van Berge, J.W. Niemantsverdriet, Appl. Catal. A-Gen. 312 (2006) 12.
[28] J. van de Loosdrecht, B. Bazhinimaev, J.A. Dalmon, J.W. Niemantsverdriet, S.V. Tsybulya, A.M. Saib, P.J. van Berge, J.L. Visagie, Catal. Today 123 (2007) 293.
[29] H. Karaca, O.V. Safonova, S. Chambrey, P. Fongarland, P. Roussel, A. Griboval-Constant, M. Lacroix, A.Y. Khodakov, J. Catal. 277 (2011) 14.
[30] M. Rønning, N.E. Tsakoumis, A. Voronov, R.E. Johnsen, P. Norby, W. Van Beek, Ø. Borg, E. Rytter, A. Holmen, Catal. Today 155 (2010) 289.