



	Experiment title: In situ Study of Genesis of Cobalt Oxide and Metal Nanoparticles in Silica-Supported Fischer-Tropsch Catalysts	Experiment number: CH 1821
Beamline: BM26A	Date of experiment: from: 12 November to: 16 November 2004	Date of report: 13/07/2005
Shifts: 9	Local contact(s): Sergey Nikitenko	<i>Received at ESRF:</i>
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Report:

Summary. New valuable information about the formation of nanoparticles of metallic cobalt and cobalt oxide during oxidative and reductive pretreatments of cobalt silica supported Fischer-Tropsch catalysts has been obtained during the X-ray absorption experiments performed in November 2004. A new X-ray absorption cell dedicated to *in situ* and *operando* experiments in heterogeneous catalysis was built and successfully tested for *in situ* characterization of cobalt silica supported catalysts.

Two papers have been written and accepted for publication.

The objective of the present proposal is to characterize by *in situ* XANES/EXAFS the evolution of cobalt local coordination during transformation of cobalt salts supported by silica into small clusters of cobalt oxides or cobalt silicate and then into cobalt metal particles during oxidative and reductive pretreatments of cobalt silica supported Fischer-Tropsch catalysts. A new *in situ* X-ray absorption cell designed in our laboratory was used for data collection.

The cobalt promoted and unpromoted catalysts were prepared by aqueous (co)-impregnation using cobalt nitrate or acetate, ruthenium nitrosyl nitrate or perrhenic acid. Cab-osil M-5 fumed silica ($S_{BET}=214$ m²/g) was used as catalytic support in all catalyst preparations. Prior to impregnation Cab-osil M5 was agglomerated by wetting and dried at 373 K. The precursors of promoters are ruthenium nitrosyl nitrate in HNO₃ (Ru=1.5 wt. %) or perrhenic acid. They were used as a co-impregnating salt for preparation of promoted catalysts. The contents of cobalt and promoting noble metal in the catalysts were respectively 8-10 wt. % and 0.1-0.2 wt. % .

Two types of experiments were carried out. First, the X-ray absorption spectra at Co K-edge of the eight cobalt catalysts precalcined in our laboratories and of five cobalt reference compounds were measured.

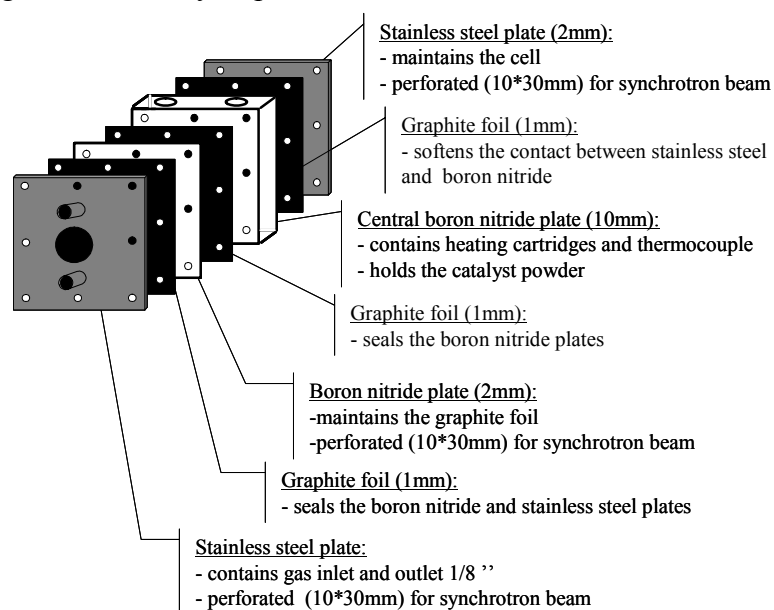


Figure 1. New experimental cell for *in situ* X-ray absorption measurements.

Then, the *in situ* decomposition of cobalt precursor and the *in situ* reduction of oxidized cobalt species in three cobalt catalysts were carried out at Co K-edge using our new *in situ* X-ray absorption cell (Figure 1). Below is a brief description of the new X-ray cell. The cell consists of several plates of stainless steel and boron nitride linked together using graphite seals. The components of the cell are held together with 8 screws. The use of homemade plates of boron nitride (made from bulk boron nitride - MCSE, Grade A) allows minimizing X-ray absorption by the cell. To reduce further X-ray absorption by boron nitride at lower photon energies (~7keV) the length of the beam path in boron nitride has to be reduced and the plate was drilled from the rear side. To perform X-ray absorption measurements, the plates of boron nitride and stainless steel have to be assembled and sealed using graphite foils of 2 mm thickness (Carbone Lorraine). Our experiments have shown that the cell is leak-free at atmospheric pressure in pure oxygen or pure hydrogen at temperatures respectively from ambient to 623 and 673 K. The catalyst for X-ray absorption measurements in the form of compacted powder is loaded in the hollow of the plate of boron nitride. The cell is equipped with a system of gas circulation, thermocouple and heating elements. Two holes were drilled on each of boron nitride plates and graphite foils (Figure 1) to constitute the gas flow channel (one for inlet and the other for outlet). The gas flow from the top to the bottom through the catalyst powder is essential in the design of cells for *in situ* or *operando* X-ray absorption measurements. The cell is heated by two heating cartridges placed inside the boron nitride plate (sample holder, Figure 2). Due to the high thermal conductivity (30-100 W/m K) of boron nitride, the heat is supplied uniformly to the catalyst. In order to ensure good thermal contact, the thermocouple is placed close to the catalyst sample in a hole drilled in the boron nitride plate. The *in situ* cell operates with a programmable temperature controller, which enables performing well-controlled temperature ramps in the range 293-673 K, with very low temperature gradients (< 1 K). The cell can be shielded and continuously purged with nitrogen if hydrogen or any other explosive gases are used.

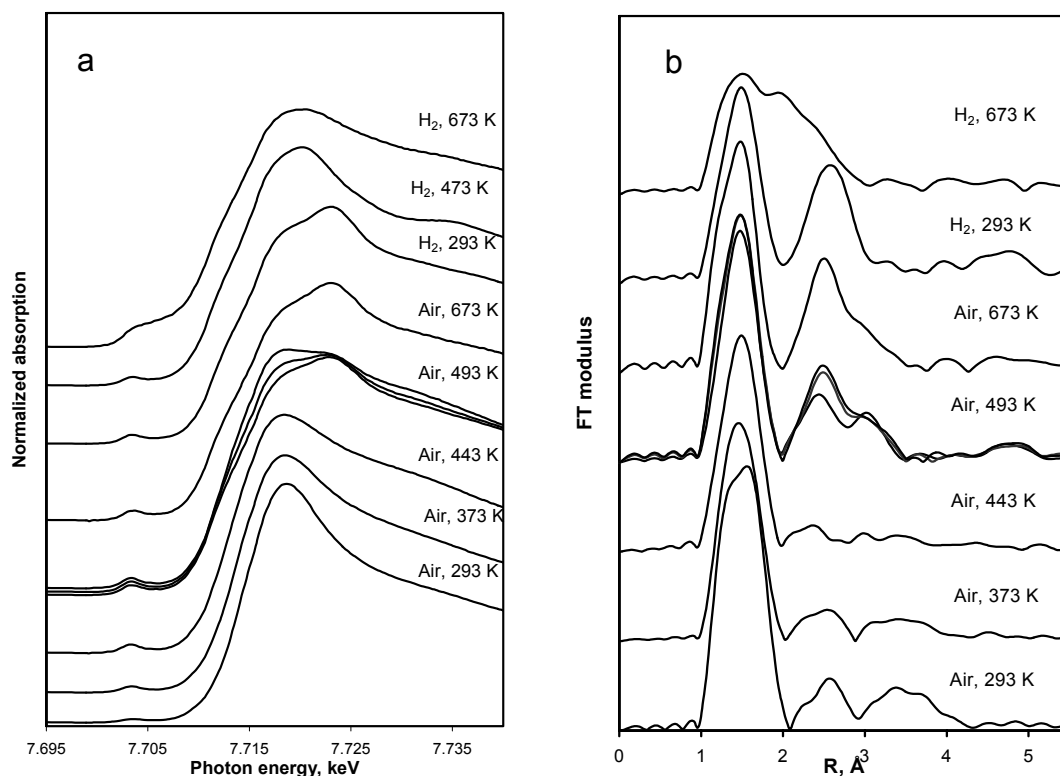


Figure 2. *In situ* XANES spectra (a) and moduli of Fourier transform of EXAFS (b) of cobalt catalyst prepared using impregnation with cobalt acetate and ruthenium nitrosyl nitrate. The spectra were measured *in situ* during the decomposition of cobalt precursor in the flow of air and reduction in hydrogen.

The representative *in situ* XANES spectra and Fourier transform EXAFS moduli for cobalt supported catalysts acquired using the new X-ray cell during the pretreatments in the flow of air and in the flow of hydrogen at different temperatures are shown in Figure 2. The data display major evolution of cobalt local coordination during the pretreatments. The quality of X-ray absorption data was excellent, much better than in our previous experiments at cobalt K-edge, which involved the synchrotron beam generated by LURE (Orsay).

The X-ray absorption results were analyzed using crystalline cobalt acetate, cobalt nitrate hydrates, Co₃O₄, CoO, Co foil, α - and β -cobalt silicate as standard compounds. X-ray absorption study showed that in both unpromoted and Ru and Re-promoted cobalt catalysts after impregnation and drying, cobalt is present mainly in octahedrally coordinated complexes. Decomposition of octahedrally coordinated cobalt complexes leads to easily reducible crystallites of Co₃O₄ and amorphous cobalt silicate. The repartition of cobalt species between Co₃O₄ and cobalt silicate depends essentially on the exothermicity and temperature of decomposition of precursor decomposition. Cobalt nitrate precursor, with an endothermic decomposition, favors Co₃O₄ crystallites. Cobalt acetate precursor, with an exothermic decomposition, favors cobalt silicate. Slow decomposition of cobalt acetate at low temperatures (443-493 K) results in the fraction of cobalt silicate being decreased. This favors the more reducible Co₃O₄ phase. For the catalysts prepared from cobalt nitrate, promotion with ruthenium results in smaller Co₃O₄ particle sizes, while maintaining high reducibility after treatment with hydrogen at 400°C. For the catalyst prepared via low temperature decomposition of cobalt acetate, addition of ruthenium increases the fraction of Co₃O₄ crystalline phase and decreases the concentration of barely reducible cobalt silicate and thus enhances cobalt reducibility and the number of cobalt metal sites.

Two papers were accepted for publication:

- Optimization of the pretreatment procedure in the design of cobalt silica supported Fischer-Tropsch catalysts by J.S. Girardon, A. Constant-Griboval, L. Gengembre, P.A. Chernavskii and A.Y. Khodakov, *Catalysis Today*, in the press.
- A new experimental cell for *in situ* and *operando* X-ray absorption measurements in heterogeneous catalysis by J.S. Girardon, A.Y. Khodakov, M. Capron, S. Cristol, C. Dujardin, F. Dhainaut, S. Nikitenko, F. Meneau, W. Bras, and E. Payen, *Journal of Synchrotron Radiation*, in the press.