



	<b>Experiment title:</b> Effect of sucrose and other organic compounds on the structure of cobalt species in the reduced and oxidized silica-supported Fischer-Tropsch catalysts	<b>Experiment number:</b> CH-2210
<b>Beamline:</b>	<b>Date of experiment:</b> from: 26/04/2006 to: 30/04/2006	<b>Date of report:</b> 26/02/2007
<b>Shifts:</b>	<b>Local contact(s):</b> Dr. S. NIKITENKO	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Dr. Andrei KHODAKOV* Dr Wei CHU* Mr Jean-Sébastien GIRARDON Dr. Anne GRIBOVAL-CONSTANT Dr. Pascal FONGARLAND*  All applicants are from the Unité de Catalyse et de Chimie du Solide, UMR 8181 CNRS, Bât. C3, USTL, Cité scientifique, 59655 Villeneuve d'Ascq, France		

## Report:

### Summary.

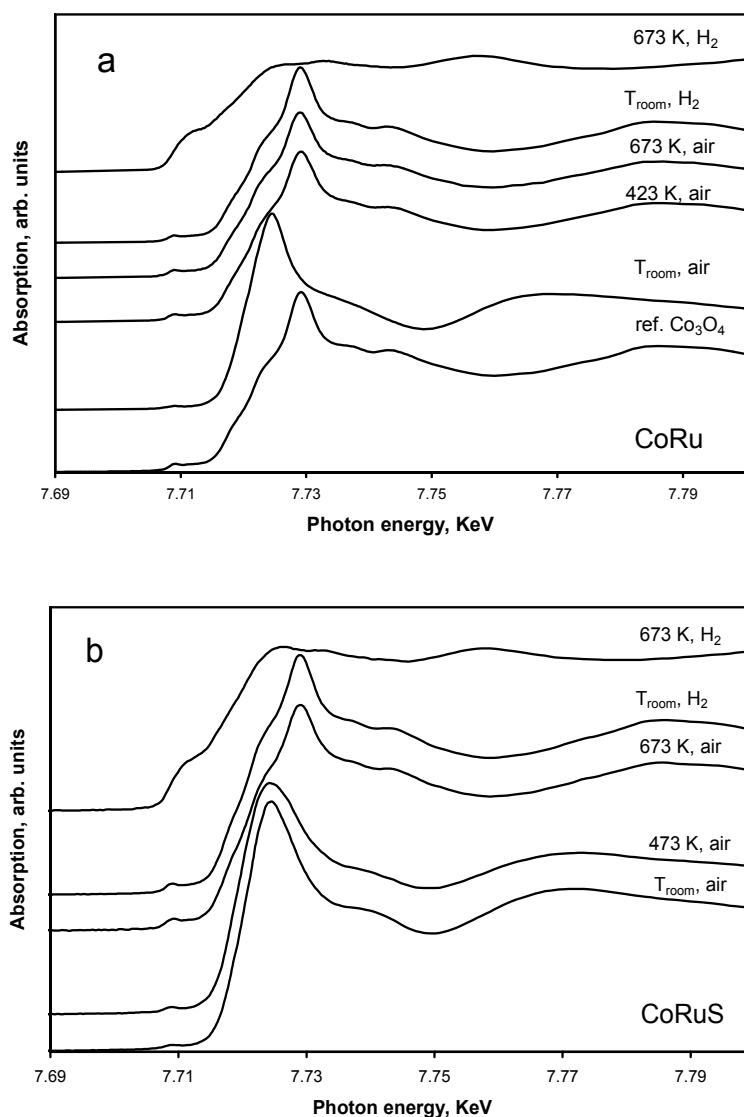
The experiments provided new data about the structure of cobalt species and genesis of active sites in cobalt silica supported catalysts prepared with addition of sucrose. Mononuclear octahedral cobalt complexes were observed in the catalysts after impregnation and drying. It was shown that genesis of cobalt dispersion proceeded during catalyst calcination in air. Decomposition of cobalt nitrate and crystallization of cobalt oxide seem to be the crucial steps in the preparation of highly dispersed cobalt catalysts. Addition of sucrose modifies the structure of supported cobalt complexes and influences the crystallization of supported cobalt oxide. This leads to higher crystallization temperatures and to the catalysts with extremely high cobalt dispersion. Addition of sucrose during impregnation, while significantly enhancing cobalt dispersion, does not diminish cobalt reducibility.

The objective of the proposal CH-2210 is to characterize by *in situ* XANES/EXAFS the evolution of cobalt local coordination during preparation of cobalt Fischer-Tropsch catalysts prepared with addition of sucrose. Our previous results have shown that the ruthenium and rhenium promoted catalysts, which were prepared using sucrose addition, have the highest number of cobalt metal surface sites and possess high activity in Fischer-Tropsch synthesis.

Cobalt catalysts were synthesized via incipient wetness impregnation or co-impregnation using aqueous solutions of cobalt nitrate and promoters. Cab-o-sil M-5 fumed silica ( $S_{\text{BET}}=214 \text{ m}^2/\text{g}$ , Cabot) was used as catalytic support in all catalyst preparations. Prior to impregnation, Cab-o-sil M5 was agglomerated by wetting and dried at 373 K. The precursors of noble metal promoters were either a commercial solution of ruthenium nitrosyl nitrate in  $\text{HNO}_3$  (Ru=1.5 wt. %, Sigma-Aldrich) or an aqueous solution of perrhenic acid ( $\text{HReO}_4$ , Sigma-Aldrich). In several preparations the impregnating solutions also contained sucrose with the Co/sucrose molar ratio of 10. The contents of cobalt and promoting noble metal (Ru or Re) in the catalysts were respectively 8-10 wt.% and 0.1-0.2 wt.%. The impregnated catalysts were dried in an oven, calcined in a flow of air at different temperatures (373-673 K) and then reduced in hydrogen at 673 K for 5 h. The rates of temperature ramping during the calcination and reduction were respectively 1 and 3.3 K/min. The catalysts are labeled as CoMT(S), where M designates the promoting metal (Ru or Re), T and (S) indicate respectively the temperature of catalyst calcination and eventual addition of sucrose during impregnation.

The impregnated and dried cobalt catalysts (prior to calcination at  $T \geq 373 \text{ K}$ ) are designed as CoMD(S).

Two types of experiments were carried out. First, the X-ray absorption spectra at Co K-edge of cobalt catalysts precalcined in our laboratories and cobalt reference compounds were measured. Then, the *in situ* decomposition of cobalt precursor and the *in situ* reduction of oxidized cobalt species in cobalt catalysts prepared with and without sucrose addition were carried out at Co K-edge using our new *in situ* X-ray absorption cell. The measurements were performed in transmission mode; two ionization chambers were used for X-ray detection. The Si (111) double-crystal monochromator was calibrated by setting the first inflection point of K-edge spectrum of Co foil at 7709 eV. The time of measuring an X-ray absorption spectrum (7600-8400 eV) was about 30-40 min. The X-ray absorption data were analyzed using the conventional procedure. The XANES spectra after background correction were normalized by the edge height. After subtracting metal atomic absorption, the extracted EXAFS signal was transformed without phase correction from  $k$  space to  $r$  space to obtain the radial distribution function (RDF). Crystalline  $\text{Co}_3\text{O}_4$ ,  $\text{CoO}$ , Co foil,  $\alpha$ - and  $\beta$ -cobalt silicate were used as reference compounds for XANES and EXAFS



**Figure 1.** *In situ* XANES spectra measured for CoRu catalysts prepared without (a) and with (b) sucrose addition under flow of air and hydrogen at different temperatures. The spectra are offset for clarity.

data analysis.

The characteristic XANES spectra and Fourier transform moduli of EXAFS for catalysts prepared with and without addition of sucrose are shown in Figure 1 and 2. The XANES of both impregnated and dried CoRuD and CoRuD(S) catalysts are almost identical to that of cobalt nitrate (Figure 1, curves “ $T_{\text{room}}$ , air”). The EXAFS Fourier transform moduli (Figure 2, curves “ $T_{\text{room}}$ , air”) show an intense peak at 1.6 Å, which is related to Co-O coordination shell in cobalt nitrate. No cobalt atoms are observed in the second cobalt coordination shell. Figures 1 and 2 show that calcination of CoRuD catalyst at 423 K results in decomposition of cobalt nitrate. The XANES and EXAFS Fourier transform modulus of CoRuD catalysts after heating in air at 423 K are almost identical to those of  $\text{Co}_3\text{O}_4$ , while calcination of CoRuD(S) samples

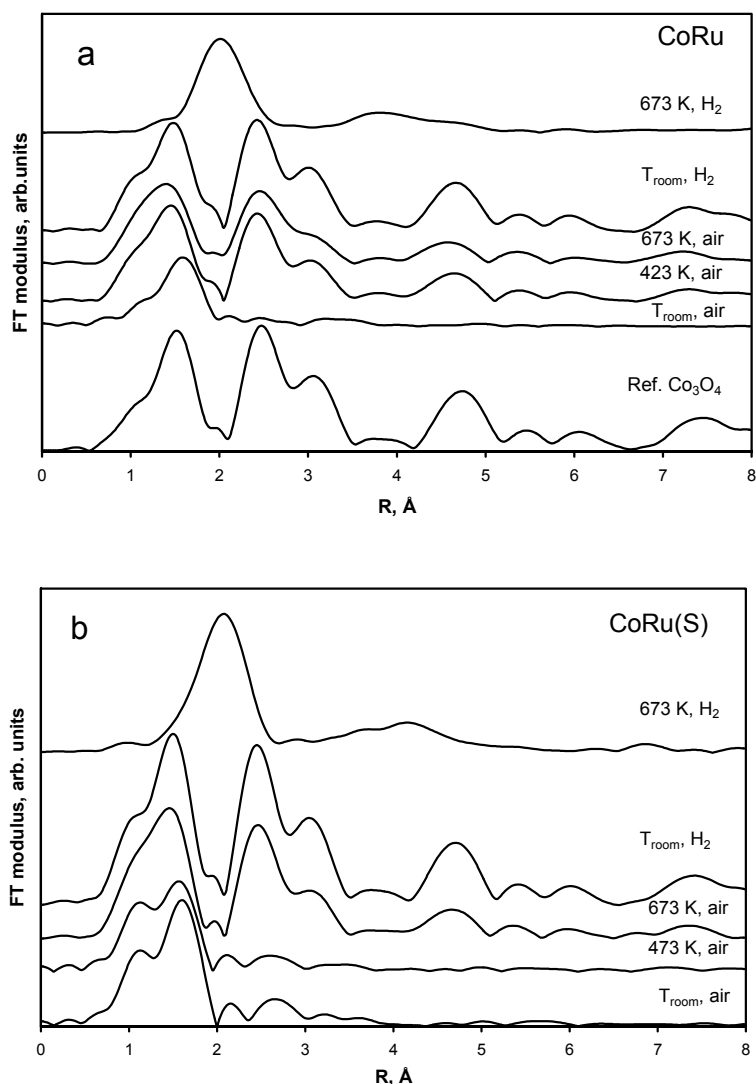
even at 473 K does not result in any noticeable modification of Co adsorption edge and EXAFS Fourier transform modulus. This supposes higher temperatures of decomposition of cobalt complexes and crystallization of  $\text{Co}_3\text{O}_4$  phase in the catalysts prepared with sucrose addition than in the catalysts prepared without sucrose. In other words, sucrose addition to cobalt silica supported FT catalysts seems to alter the mechanism of decomposition of cobalt nitrate and to affect nucleation and crystallization of resulting cobalt oxide species.

While the XANES spectra of CoRu373(S) and CoRe373(S) (not shown) are almost identical to the XANES spectra of cobalt nitrate, the XANES spectra for the CoRu673, CoRe673, CoRu673(S) and CoRe673(S) catalysts indicate the presence of  $\text{Co}_3\text{O}_4$ .

CoRuD(S) and CoRuD catalysts precalcined and then reduced in hydrogen at 673 K have almost identical XANES spectra and EXAFS Fourier transform moduli (Figure 1 and 2). Both of them are characteristic of metallic cobalt. Thus, X-ray absorption data for these catalysts indicate high extent of cobalt reduction. Important observation is that addition of sucrose during impregnation, while dramatically enhancing cobalt dispersion, does not diminish cobalt reducibility.

## Publications :

1. J.-S. Girardon, E. Quinet, A. Griboval-Constant, P.A. Chernavskii, L. Gengembre and A. Y. Khodakov, Cobalt Dispersion, Reducibility and Surface Sites in Promoted Silica Supported Fischer-Tropsch Catalysts, *J. Catalysis*, **2007**, accepted, in the press.
2. A.Y. Khodakov, W. Chu, J.-S. Girardon, P.A. Chernavskii, A. Constant-Griboval, Design of cobalt supported Fischer-Tropsch catalysts using unconventional preparation methods, *Proceedings 8<sup>th</sup> Natural Gas Conversion Symposium*, May 27-31, Natal, Brazil.



**Figure 2.** *In situ* EXAFS Fourier transform moduli measured for CoRu catalysts prepared without (a) and with (b) sucrose addition under flow of air and hydrogen at different temperatures. The moduli are offset for clarity.