



	Experiment title: <b>Investigation of cobalt nanoparticles and cobalt amorphous phases in plasma assisted cobalt silica supported Fischer-Tropsch catalysts</b>	Experiment number: <b>CH- 2764</b>
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<b>Shifts:</b> 12	<b>Local contact(s):</b> Dr. Sergei Nikitenko (email: <a href="mailto:nikitenko@esrf.fr">nikitenko@esrf.fr</a> )	<i>Received at ESRF:</i>

**Names and affiliations of applicants (\* indicates experimentalists):**

Dr Andrei KHODAKOV\*, Unité de Catalyse et de Chimie du Solide, Villeneuve d'Ascq, France  
Dr. Anne GRIBOVAL-CONSTANT, Unité de Catalyse et de Chimie du Solide, Villeneuve d'Ascq, France  
Ms. Jingping HONG\*, Unité de Catalyse et de Chimie du Solide, Villeneuve d'Ascq, France  
Dr. Pascal FONGARLAND, Unité de Catalyse et de Chimie du Solide, Villeneuve d'Ascq, France  
Mr. Alan JEAN-MARIE\*, Unité de Catalyse et de Chimie du Solide, Villeneuve d'Ascq, France  
Professor Stanislas PIETRZYK, Unité de Catalyse et de Chimie du Solide, Villeneuve d'Ascq, France

**Report:  
Summary.**

The genesis of cobalt metal phase (active for Fischer-Tropsch synthesis) was investigated in cobalt monometallic, Ru and Ir-promoted alumina and silica supported catalysts using in situ XANES/EXAFS. The catalysts were prepared using aqueous impregnation with cobalt nitrate. The cobalt precursor in the catalysts was decomposed using glow discharge and high temperature plasma with a wide range of intensity. Some residual concentration of cobalt nitrate was detected in the plasma pretreated samples. The experiments have shown that pretreatment with glow discharge plasma does not affect the concentration of barely reducible cobalt silicate in silica supported catalysts. In-situ XAS data suggest that smaller cobalt particles in the plasma-assisted monometallic cobalt catalysts displayed more difficult cobalt reducibility than larger cobalt particles in the conventionally calcined counterparts. Promotion with ruthenium and iridium resulted in a significant increase in cobalt reducibility in both plasma-assisted and conventionally calcined catalysts. In silica supported catalysts, the concentration of cobalt silicate has increased after catalyst reduction in hydrogen relative to the oxidized samples. This suggests that some cobalt silicate possibly forms during catalyst reduction in addition to cobalt silicate already present in the catalysts after calcination. Due to the synergism between high cobalt dispersion and good cobalt reducibility, Ru-promoted plasma-assisted cobalt catalysts exhibited higher fraction of cobalt metal active phase for Fischer-Tropsch reaction.

Fischer-Tropsch (FT) synthesis converts natural gas-, coal- and biomass-derived syngas into liquid hydrocarbon fuels which are totally free of sulfur- and nitrogen-containing compounds and have very low aromatic contents. FT synthesis proceeds on cobalt metal sites. The overall number of cobalt metal sites on supported catalysts depends on both cobalt dispersion and reducibility. Higher cobalt dispersion results in a large number of cobalt metal sites. In monometallic cobalt catalysts however, an increase in cobalt dispersion is often accompanied by a drop in cobalt reducibility. Indeed, smaller cobalt particles are usually more difficult to reduce than larger ones. In addition, very small cobalt particles in highly dispersed catalysts could

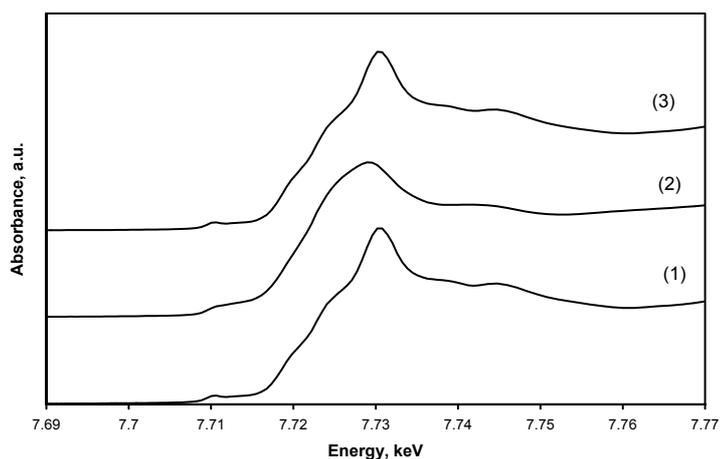


Figure 1. XANES spectra of calcined (1), plasma-jet pretreated and calcined Co-Ir/Al<sub>2</sub>O<sub>3</sub> catalysts and reference Co<sub>3</sub>O<sub>4</sub>.

interact strongly with support. This leads to the formation of mixed oxides (i.e., cobalt silicates in the case of Co/SiO<sub>2</sub> catalysts), which are difficult to reduce and inactive for FT synthesis. Use of catalyst promoters such as noble metals can break this dispersion-reducibility dependence in supported catalysts. Plasma is an ionized gas that can be generated by a number of methods, including electric discharges (glow, microwave, plasma jet, radio frequency). Glow discharge plasma is a kind of non-thermal plasma, which is characterized by high electron temperature (10,000–100,000 K) and relatively low gas temperature. Plasma intensity is determined by the applied power in terms of electric voltage and the gap between two electrodes. The energetic species (electrons, ions and radicals) in the plasma could modify the catalyst surface, particle size and morphology of active phase, as well as active phase-support interactions in the catalysts.

No information about the influence of plasma on metal dispersion and catalytic performance of silica-supported cobalt FT catalysts is available in the literature. In this experiment, a series of silica-supported cobalt based catalysts were prepared by glow-discharge plasma with different plasma power voltages (which correspond to different plasma intensities). The objective of the experiment is evaluate the fractions of different cobalt species (Co<sub>3</sub>O<sub>4</sub>, CoO, partially decomposed cobalt nitrate complexes, amorphous cobalt silicate) in monometallic, Ru and Ir-promoted silica and alumina supported Fischer-Tropsch catalysts at different steps of catalyst preparation using X-ray absorption (XANES and EXAFS).

The oxidized catalysts were analyzed by X-ray absorption spectroscopy at the cobalt K absorption edge. The XANES spectra and EXAFS Fourier transform moduli of both oxidized monometallic and ruthenium promoted silica-supported cobalt catalysts were similar to those of the Co<sub>3</sub>O<sub>4</sub> reference compound. In agreement with XRD data, this suggests that Co<sub>3</sub>O<sub>4</sub> is the major cobalt phase in both conventionally calcined and plasma-assisted catalysts. For a more quantitative analysis, the XANES spectra were fitted using a linear combination of XANES spectra of reference compounds. The XANES data were indicative of the presence

of both  $\text{Co}_3\text{O}_4$  and  $\alpha$ -cobalt silicate, while no residual cobalt nitrate was detected. Thus, the XANES analysis suggests that decomposition of cobalt nitrate in both conventional and plasma-assisted cobalt catalysts was nearly complete after calcination at 523 K for 5 h.  $\text{Co}_3\text{O}_4$  content was higher than 85% in both conventional and plasma-assisted samples. No noticeable effect of plasma intensity on the fraction of cobalt silicate was observed. In plasma jet treated Co-Ir- $\text{Al}_2\text{O}_3$  samples some concentration of cobalt nitrate was however detected even after plasma treatment (Figure 1).

Figure 2 shows XANES spectra of Co/ $\text{SiO}_2$  and CoRu/ $\text{SiO}_2$  catalysts and their plasma-assisted counterparts reduced in hydrogen at 673 K. The experiments were conducted using our in situ XAS cell (J.-S. Girardon, J. Synchrotron Rad., 2005). Both XANES spectra and Fourier transform moduli were different for conventionally calcined and plasma-assisted samples. Note that the differences in the XANES region could be related to the changes in both electronic properties (oxidation state) and local coordination of the absorbing atoms. The extent of cobalt reduction in silica-supported cobalt catalysts seems to be a function of plasma pretreatment and promotion with ruthenium. The XANES curves were fitted using a linear combination of XANES spectra of metallic cobalt, CoO,  $\alpha$ - $\text{Co}_2\text{SiO}_4$  and  $\beta$ - $\text{Co}_2\text{SiO}_4$  as reference compounds. The fitting showed a much higher content of CoO and a much lower fraction of metallic cobalt in the plasma-assisted cobalt catalysts compared to the conventionally calcined counterparts. Plasma pretreatment seems to affect cobalt reducibility in both monometallic and Ru-promoted catalysts. Another interesting observation is that the concentration of cobalt silicate has increased after catalyst reduction in hydrogen at 673 K relative to the oxidized samples. This suggests that some cobalt silicate possibly forms during catalyst reduction in

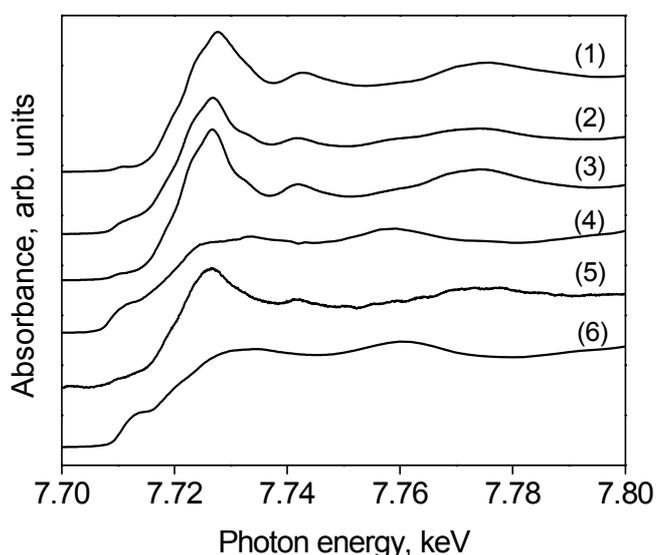
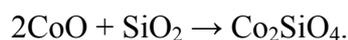


Figure 2. In-situ XANES spectra for (1) CoO, (2) reduced Co/ $\text{SiO}_2$ , (3) reduced Co/ $\text{SiO}_2$ -P60, (4) reduced CoRu/ $\text{SiO}_2$ , (5) reduced CoRu/ $\text{SiO}_2$ -P60 and (6) metallic cobalt. In the Co/ $\text{SiO}_2$ -P60 and CoRu/ $\text{SiO}_2$ -P60 cobalt precursor was decomposed using glow discharge plasma

addition to cobalt silicate already present in the catalysts after calcination. The cobalt silicate fraction was more significant in the monometallic catalysts which are more difficult to reduce and which contain higher fraction of CoO phase than in Ru-promoted samples. At the higher reduction temperature, CoO phase probably reacts with  $\text{SiO}_2$  yielding cobalt silicate compounds:



Water produced during reduction of cobalt oxide could also play a role in cobalt silicate formation during catalyst reduction.

Two articles have been submitted (Journal of Catalysis, Applied Catalysis A).