



	Experiment title: In situ study of the effect of water and hydrogen on the stability of cobalt nanoparticles in cobalt supported Fischer-Tropsch catalysts	Experiment number: CH-2434
Beamline:	Date of experiment: from: 05 April to: 10 April 2007	Date of report: 25/02/2008
Shifts: 12	Local contact(s): Dr Sergey NIKITENKO (e-mail: nikitenko@esrf.fr)	<i>Received at ESRF:</i>
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Report:

Summary. The oxidation state of cobalt in the pre-reduced cobalt alumina supported Fischer-Tropsch catalysts was studied in situ during exposure to humid argon and hydrogen at 220°C and atmospheric pressure. It was found that pretreatment with humid argon resulted in rapid oxidation of cobalt metallic nanoparticles, while no modification of cobalt metallic phase was observed by in situ XANES/EXAFS at wide range of H₂O/H₂ ratios. This suggests that no bulk oxidation of metallic cobalt proceeds in humid hydrogen at 220°C and atmospheric pressure. It appears that the oxidation state of cobalt during FT reaction is strongly affected by the reaction conditions. Accomplishment of the proposal has led to three publications. The first paper has been published in Journal of Catalysis. The second paper has been submitted to Angew. Chem. Int Ed. The third paper will be shortly submitted to Applied Catalysis A.

In recent publications [1, 2] we have proposed a comprehensive kinetic model of FT synthesis on cobalt catalysts based on the detailed reaction mechanism. The model gives explicit relations between the rates of carbon monoxide conversion and hydrocarbon production from one hand and H₂, CO, water or olefin concentrations from another hand. The proposed quantitative kinetic model however, does not take into account deactivation of the catalyst during the reaction. Several authors [3,4] have shown that FT reaction rate drops faster at higher water concentrations. Our previous report [1] has demonstrated that at moderate water levels ($C_{H_2O}^L / C_{H_2}^L < 4$ corresponding to $P_{H_2O} / P_{H_2} < 0.4$), the catalyst deactivation is reversible; the catalytic activity can be regenerated by decrease in the concentration of water and increase in conversion of hydrogen at a given temperature. The mechanism of reversible deactivation of FT catalysts by water may be represented by:



where * and *-O indicate respectively a reduced and an oxidized cobalt species.

The objective of this project was provide quantitative *in situ* information on concentration of oxidized and reduced cobalt species during pretreatment in humid mixtures with different H₂O/H₂ ratios at atmospheric pressure.

Cobalt catalysts were impregnated using aqueous solutions of cobalt nitrate and Puralex SCCA-5/170 γ -alumina ($S_{BET}=165 \text{ m}^2/\text{g}$, pore diameter of 8.3 nm and total pore volume of 0.477 cm³/g, Sasol). For preparation of the catalysts promoted with Pt, the impregnating solution also contained dihydrogen hexachloroplatinate. After the impregnation the catalysts were dried at 373 K in an oven. Cobalt nitrate in the studied catalysts was decomposed either by conventional calcinations in air or by treatment with glow discharge plasma. To yield the conventional cobalt alumina supported catalysts, the impregnated and dried samples were calcined in a flow of air either at 473 or at 613 K for 5 h with temperature ramp of 1 K/min. To obtain plasma assisted cobalt catalysts, the dried samples were exposed at ambient temperature to glow discharge nitrogen plasma for 45 min and then to hydrogen plasma for another 45 min. The catalysts prepared using conventional calcination contained cobalt

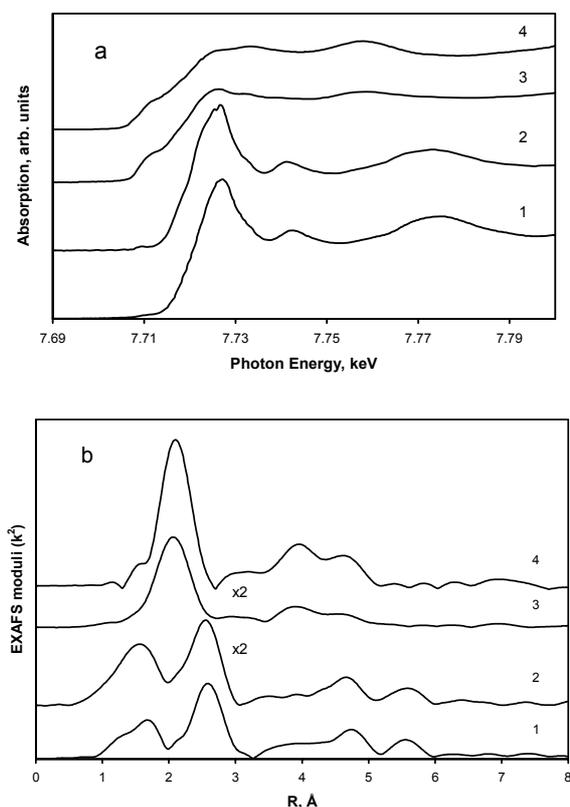


Figure 1. XANES spectra (a) and k^2 -weighted EXAFS Fourier transform moduli (b) for (1) CoO, (2) reduced monometallic catalyst ($T_{cal}=613 \text{ K}$), (3) reduced cobalt catalyst promoted with Pt ($T_{cal}=613 \text{ K}$ and (4) metallic cobalt. The reference spectra were measured at room temperature, while the spectra of the catalysts were acquired at 673 K in pure hydrogen.

particles sizes of about 9 nm, while very small cobalt oxide particles were detected in the plasma treated samples.

The operando XAS cell described elsewhere [5] was used for XAS measurements. Cobalt catalysts were reduced in a flow of hydrogen at 673 K for 5 h, the rate of temperature ramping during reduction was 3 K/min. The X-ray absorption spectra at the Co K-edge were measured in transmission mode at BM26A (Duble) beamline. The reduced catalysts were characterized *in situ* at 400°C by X-ray absorption (Figure 1). Metallic cobalt was the dominant phase in Pt-promoted catalysts, while mostly cobalt oxide species were detected in monometallic cobalt catalysts. Since very low concentrations of cobalt metal phase were observed in monometallic cobalt catalysts, most of further experiments with humid hydrogen and argon were conducted with Pt-promoted catalysts.

After reduction at 400°C, the catalyst temperature was lowered to 220°C. The catalyst was then treated at this temperature with H₂O/H₂ mixtures while continuously measuring X-ray absorption at Co K-edge. The total pressure was 1 atm, while H₂O/H₂ molar ratio in the feed varied from 3 to 30. Water was added to the hydrogen flow using a HPLC pump. The XANES spectra and EXAFS Fourier transform of the CoPt/Al₂O₃ catalyst precalcined at 340°C and reduced at 400°C are shown in Figure 2.

Addition of significant amount of water to hydrogen

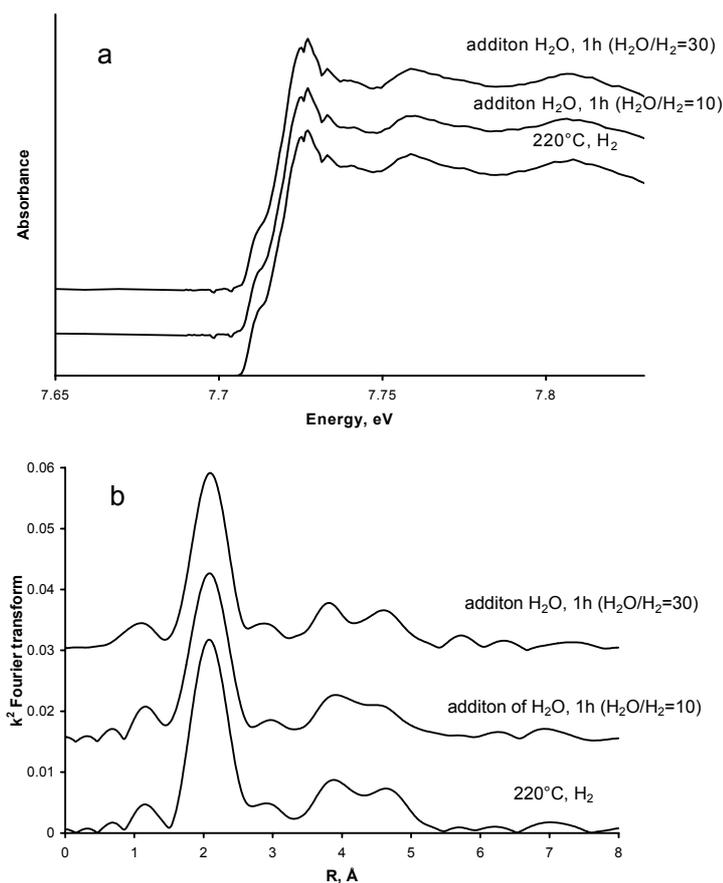


Figure 2. XANES spectra (a) and k^2 -weighted EXAFS Fourier transform moduli (b) for CoPt/ Al_2O_3 catalyst reduced at 400°C and then exposed to $\text{H}_2\text{O}/\text{H}_2$ mixtures at 220°C

flow did not to lead to modification of either XANES or EXAFS. This suggests that at atmospheric pressure even at relatively high water level no bulk oxidation of metallic cobalt by water occurs in the presence of hydrogen. No bulk cobalt oxidation was also observed with other cobalt alumina supported catalysts promoted with platinum. It should be emphasized that exposure of these catalysts at the same temperatures to $\text{H}_2\text{O}/\text{Ar}$ mixtures ($\text{H}_2\text{O}/\text{Ar}=4$) has resulted in almost complete oxidation of cobalt metal particles. Gas-chromatographic analysis of $\text{Ar}/\text{H}_2\text{O}$ mixtures did not reveal the presence of oxygen traces which might be responsible of cobalt oxidation. Thus it was suggested that small cobalt particles could be oxidized by water in the absence of hydrogen, while no bulk oxidation of cobalt by water is observed in the presence of hydrogen.

Note that XAS provides information about all cobalt atoms present in the catalysts, while the rate of FT reaction is mostly sensitive to the concentration of cobalt metallic atoms on the surface. Complementary kinetic studies carried out in our laboratories involving carbon monoxide hydrogenation at transient conditions were indicative of a decrease in the number of cobalt metal sites in the CoPt/ Al_2O_3 catalysts pretreated with $\text{H}_2\text{O}/\text{H}_2$ mixtures at the conditions similar to those used in the ESRF. It was suggested that

pretreatment of cobalt catalyst with $\text{H}_2\text{O}/\text{H}_2$ could result in partial oxidation of the catalyst surface while no bulk oxidation of cobalt metal particles has occurred.

This proposal has resulted in three publications:

1. Chu, W., Chernavskii, P.A., Gengembre, L., Pankina, G.A., Fongarland, P., Khodakov, A.Y. Cobalt species in promoted cobalt alumina-supported Fischer-Tropsch catalysts. *J. Catal.* **2007**, 252 (2), 215-230.
2. Chu, W., Wang, L.-N., Chernavskii, P. A. and Khodakov, A. Y. Glow discharge plasma assisted design of cobalt catalysts for Fischer Tropsch synthesis. *Angew. Chem. Inter. Ed.*, Submitted
3. Fongarland, P., Hong, J., Nikitenko S. and Khodakov, A.Y. Effect of water on the structure of cobalt Fischer-Tropsch catalysts, in preparation.

Reference

- 1 Bremaud, M., Fongarland, P., Anfray, J., Jallais, S., Schweich D. and Khodakov, A.Y, *Catal. Today*, **2005**, 106, 137.
- 2 Anfray, J., Bremaud, M., Fongarland, P., Khodakov, A., Jallais, S., Schweich, D. *Chem. Eng. Sci.* **2007**, 62 (18-20 SPEC. ISS.), 5353.
- 3 Jacobs, G., Patterson, P.M., Zhang, Y., Das, T., Li, J., Davis, B.H. *Appl. Catal. A* **2002**, 233, 215.
- 4 Saib, A.M., Borgna, A., van de Loosdrecht, J., van Berge, P.J., Geus, J.W., Niemantsverdriet, J.W. *J. Catal.* **2006**, 239, 326.
- 5 Girardon, J.S., Khodakov, A.Y., Capron, M., Cristol, S., Dujardin, C., Dhainaut, F., Nikitenko, S., Meneau, F., Bras, W. and Payen, E. *J Synchrotron Radiation*, **2005**, 12, 680.