



	Experiment title: Operando XAS/XRD/Raman investigation of cobalt active phases in alumina supported catalysts at the real conditions of Fischer-Tropsch synthesis	Experiment number: CH- 2692
Beamline: BM01B	Date of experiment: from: 5 Nov 2008 to: 11 Nov 2008	Date of report:
Shifts: 18	Local contact(s): Dr. Olga Safonova (email: safonova@esrf.fr)	<i>Received at ESRF:</i>

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Report:

Summary.

The structure of cobalt alumina and silica supported catalysts was studied during Fischer-Tropsch synthesis using a combination of synchrotron based time-resolved X-ray diffraction and X-ray absorption. To the best of our knowledge, this report represents the first study of cobalt catalysts performed at the realistic conditions of Fischer-Tropsch synthesis (high pressure and temperature). Cobalt sintering and carburization seem to be major mechanisms of deactivation of cobalt alumina supported catalysts during the first hours of Fischer-Tropsch synthesis. No cobalt oxidation was detected at these experimental conditions. The accomplishment of the proposal has led to two publications submitted to Angew. Chem. Int Ed and Journal of Catalysis. An abstract was submitted to the 9th European congress on catalysis (Europacat 9).

Fischer-Tropsch synthesis produces hydrocarbons from syngas which is a mixture of hydrogen and carbon monoxide. The reaction proceeds on cobalt metal particles dispersed on an oxide support [1]. The reaction rate typically decreases with time-on-stream. The most significant drop in the reaction rate has been usually observed during the first hours of the reaction. The available information about deactivation of cobalt catalysts during Fischer-Tropsch reaction is rather contradictory [1, 2]. Several phenomena are usually evoked [1]: cobalt oxidation by water produced by the reaction, formation of cobalt aluminate or silicate, carbidization, coking, cobalt sintering, cobalt dissolution in organic acids, catalyst loss due to the generation of ultra fine particles... The large discrepancies in literature on the deactivation behavior are likely due to the lack of direct characterization of cobalt catalysts [2]. The indirect methods of catalyst characterization do not seem to provide reliable information about the catalyst structure, which could alter after catalyst withdrawn from the reactor. Direct *in-situ* characterization of the evolution of catalyst structure in Fischer-Tropsch reaction represents a significant challenge because of harsh reaction conditions: high temperature, high pressure, multiphase medium... The present work has addressed an *in-situ* study of cobalt catalysts performed at the realistic conditions of Fischer-Tropsch synthesis using a combination of synchrotron based X-ray diffraction and X-ray absorption. To the best of our knowledge, this report represents the first *in-situ* investigation of Fischer-Tropsch catalysts performed at the realistic conditions (high pressure and temperature). In this paper, many difficulties due to high reaction pressures and temperatures characteristic of Fischer-Tropsch synthesis have been overcome by using the unique in-situ setup recently developed by the Swiss-Norwegian Beamline (BM10B).

Cobalt alumina and silica supported catalysts (10-25 wt. % Co and 0.1 wt. % Pt or Ru) were prepared using co-impregnation of alumina and silica supports with solutions of cobalt nitrate, tetramine platinum nitrate or

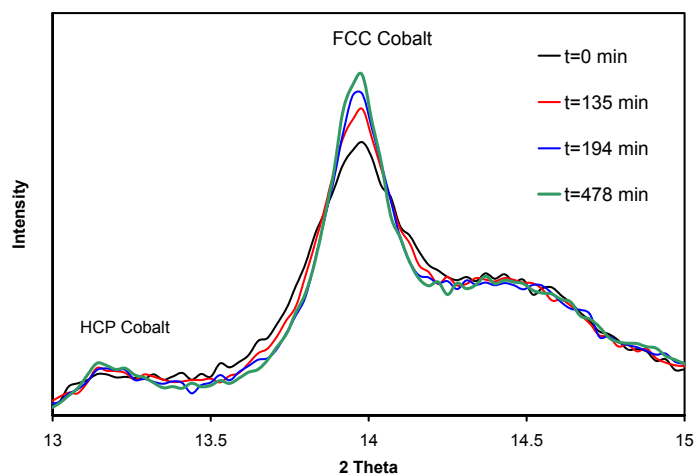


Figure 1. Evolution of *in-situ* XRD patterns with time-on-stream (0-478 min) during FT synthesis on a Co/Al₂O₃ catalyst (P=20 bars, T=220°C, H₂/CO=2). The XRD patterns indicate sintering of cobalt metallic particles

ruthenium nitrosyl nitrate. The cobalt and noble metal precursors were decomposed via calcination at 573-773 K. The catalysts were characterized using conventional BET, SEM, XRD, XPS and TPR. The performance of catalysts in FT synthesis was evaluated in a fixed bed microreactor. The *in-situ* XRD synchrotron experiments were carried out at the ESRF (SNBL beamline) at 493 K and P=20 bars using syngas with H₂/CO=2 ratio. Detection of *in-situ* XRD patterns was performed during FT reaction with simultaneous on-line analysis of gaseous reaction products by mass spectrometry.

Co₃O₄ was the major cobalt phase detected in calcined alumina supported cobalt catalysts. The size of cobalt oxide

crystallites in silica and alumina supported catalysts varied from 6 to 20 nm. Catalyst heating in hydrogen led to almost complete cobalt reduction at 350°C. In the Fischer-Tropsch fixed bed reactors, the catalysts exhibited conventional catalytic performance in FT synthesis. An example of *in-situ* synchrotron XRD data measured in syngas flow at 493 K and 20 bars with cobalt alumina supported catalysts is shown in Figure 1. The patterns are constituted by XRD peaks attributed to *fcc* and *hcp* metallic cobalt and γ -alumina. No cobalt

oxidation was detected by XRD during the initial hours of Fischer-Tropsch synthesis. The patterns slowly evolve with time-on stream, showing narrowing the peaks attributed to metallic cobalt phases, which indicates sintering of cobalt *fcc* particles from 6 to 10 nm. The *in-situ* results were consistent with post-reaction characterization of cobalt catalysts. The exposure of cobalt catalysts to syngas ($H_2/CO=2$) at longer reaction times or to syngas with lower H_2/CO ratio resulted in XRD patterns typical of Co_2C carbide compounds. These carbide compounds can be removed from the catalysts by treatment with hydrogen. Cobalt sintering and carbidization were less significant with silica supported than with alumina cobalt Fischer-Tropsch catalysts.

Cobalt sintering and carbidization seem to be major mechanisms of deactivation of cobalt alumina supported catalysts in particular during the first hours of Fischer-Tropsch synthesis.

The accomplishment of the proposal has led to two publications submitted to Angew. Chem. Int Ed and Journal of Catalysis. An abstract was submitted to the 9th European congress on catalysis (Europacat 9).

References

- [1]. Khodakov, A.Y. Chu, W. Fongarland, P. Chem. Rev. 107(2007) 1692-1704.
- [2]. van de Loosdrecht, J., Balzhinimaev, B., Dalmon, J.-A., Niemantsverdriet, J.W. , Tsybulya, S.V., Saib, A.M., van Berge, P.J., Visagie, J.L. Catal. Today 123(2007) 293-302.