

## Experiment Report Form



<b>Experiment title:</b> Genesis of cobalt nanoparticles in Fischer-Tropsch catalysts supported by carbon nanotubes	<b>Experiment number:</b> CH-2805	
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**Report:**

**Summary**

The influence of acid treatment, carbon nanotube diameter and cobalt content on the structure of cobalt catalysts supported on multi-wall carbon nanotubes, were studied using *in-situ* X-ray absorption spectroscopy and other characterization methods. The catalysts were prepared by incipient wetness impregnation using solution of cobalt nitrate assisted by sonochemical process followed by calcination in nitrogen. Characterization techniques showed the presence of smaller cobalt oxide particles of 8-10 nm diameter and irregular shape anchored to the outer surface of carbon nanotubes in the calcined samples. *In-situ* XAS showed that cobalt reducibility was slightly affected by the pretreatment with nitric acid or nanotube outer diameter. The trace amounts of nickel were detected even in the samples pretreated with nitric acid. Cobalt catalysts supported on carbon nanotubes exhibited high catalytic activity in Fischer-Tropsch synthesis. In agreement with *in-situ* XAS data relevant to reducibility and phase composition, the pretreatment with nitric acid leads to a 25% increase in hydrocarbon yield, while carbon nanotube diameter does not seem to significantly affect the Fischer-Tropsch performance of the resulting catalysts.

Cobalt catalysts supported by refractory oxides seem to be a reasonable compromise for synthesis of middle distillates and waxes because of their highly catalytic activity, stability, hydrocarbon selectivity and lower water-gas shift reaction [1]. Cobalt metal sites are generally considered as active phases for CO hydrogenation. Higher concentration of cobalt metal sites leads to an enhanced catalytic performance. For larger cobalt particles, Fischer-Tropsch specific activity is proportional to metal dispersion. Cobalt metal sites in metal particles smaller than 6-8 nm exhibit however lower intrinsic catalytic activity in Fischer-Tropsch synthesis.

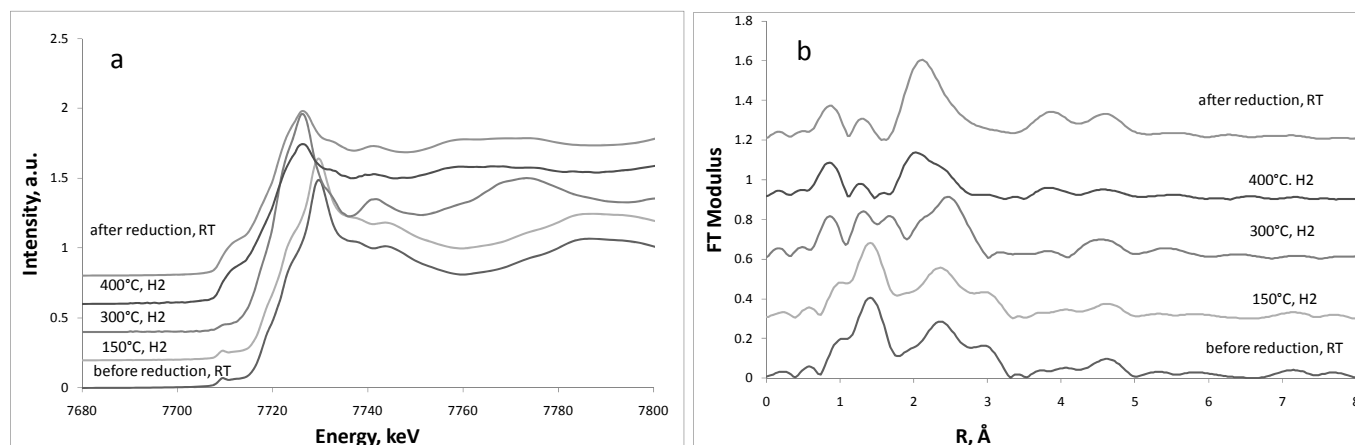
Catalytic support could also play an important role often determining the catalyst structure and catalytic performance. In addition to its influence on cobalt particle size, the interaction of cobalt with oxide supports ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ) could also result in the formation of mixed oxides (aluminate or silicate) during catalyst preparation and catalytic reaction, especially in highly dispersed catalysts. More unfortunately, these mixed oxides are not active in Fischer-Tropsch synthesis. Previously, cobalt catalysts for Fischer-Tropsch synthesis using carbon nanofibers have been prepared by de Jong et al [2] and other research groups. It was found that carbon nanofibers did not form mixed compounds with cobalt species; thus, they were used as model systems to evaluate cobalt particle size effects in Fischer-Tropsch synthesis.

Carbon nanotubes, as novel members of carbon family, present an existing interest because of their unusual mechanical and thermal stability as well as electron conductivity. The objective of the present work is to elucidate the effects due to acid treatment and carbon nanotube diameter on the structure of supported cobalt species, interaction between cobalt and carbon nanotubes and their performance in Fischer-Tropsch synthesis. A wide range of techniques were used for catalyst characterization, including *in-situ* X-ray absorption spectroscopy (XANES and EXAFS). The catalytic performance in Fischer-Tropsch synthesis was evaluated in a fixed-bed microreactor at atmospheric pressure and 20 bars.

Multi-walls carbon nanotubes prepared by chemical vapor deposition (CVD) were purchased from the CCOC company in China. Raw MWCNTs (pure  $\geq 95\%$ ) were refluxed for 5-6 h in concentrated  $\text{HNO}_3$  (54 wt %) at 353 K in an oil bath. Carbon nanotubes supported cobalt catalysts were prepared by incipient wetness impregnation using an aqueous solution of cobalt nitrate under ultrasonic conditions. The cobalt loading was 10 wt% in all the catalysts. In order to investigate the effect of carbon nanotube diameter on the structure of cobalt species, carbon nanotubes with different outer diameters (10-20 nm, 20-30nm, 30-50 nm and larger than 50 nm) pretreated with nitric acid were used as catalytic supports.

The X-ray absorption spectra at the Co K-edge were measured at the European Synchrotron Radiation Facility (DUBBLE-CRG, Grenoble, France). The measurements were performed in transmission mode, with two ionization chambers used for X-ray detection. Measuring an X-ray absorption spectrum (7600–8400 eV)

took about 30–40 min. After background correction, the XANES spectra were normalized by the edge height. Crystalline  $\text{Co}_3\text{O}_4$  and Co foil were used as reference compounds for XANES and EXAFS analysis. The typical *in-situ* XAS results are shown in Figure below. The XANES spectra and EXAFS Fourier transform moduli of a wide range of oxidized cobalt nanotubes showed that cobalt is present in the form of  $\text{Co}_3\text{O}_4$  crystallites. The spectra of supported cobalt catalyst are almost identical to that of the reference  $\text{Co}_3\text{O}_4$ .



**Figure.** *In-situ* XANES and FT EXAFS moduli of 20%Co/CNT catalysts during reduction in hydrogen at different temperatures.

In agreement with our HRTEM-EDX data, XANES showed the presence of trace amounts of nickel (Ni K absorption edge at 8.33 keV) even in the samples pretreated with conc.  $\text{HNO}_3$ . Some small activity of pure carbon nanotube in FT synthesis (in the absence of cobalt) could be possibly attributed to the presence of residual nickel.  $\text{Co}_3\text{O}_4$  reduction proceeds via formation of CoO intermediate compound. CoO forms between 150 and 300°C. Metallic cobalt in the reduced samples was detected from both XANES and EXAFS data. XAS experiments with different nanotubes showed that cobalt reducibility is only slightly affected by carbon nanotubes diameters. This result is agreement with other characterization techniques (TPR, *in-situ* magnetic) measurements. The results obtained in this project were used in the paper published by Journal of Materials Chemistry. Ref.: Zhang, H., Lancelot, C., Chu, W., Hong, J., Khodakov, A.Y., Chernavskii, P.A., Zheng, J., Tong, D. “The nature of cobalt species in carbon nanotubes and their catalytic performance in Fischer-Tropsch reaction.” *J.Mater. Chem.* 19 (2009), pp. 9241-9249.

## References

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