

## ***Report on BM26A-experiment 26-01-191***

### ***In situ EXAFS and XANES study of Mn promoted Fisher-Tropsch Co-based catalysts supported on TiO<sub>2</sub>***

In Fischer-Tropsch synthesis (FTS), supported cobalt-based catalysts are the most efficient in achieving both a high activity and selectivity towards production of high weight hydrocarbons from H<sub>2</sub>/CO syngas. However, the complexity and the large number of parameters involved both in the preparation stage (impregnation, calcination and reduction) and the FTS reaction itself explains that more than 75 years after its discovery, the nature of the active species as well as the role of the promoters in these catalysts are still debated. The FTS catalytic reaction (activity, selectivity and stability) is affected by three major factors: the dispersion of the metal phase, the extent of the reduction of the cobalt phase and the presence of a second metal used as promoter. The reducibility of the Co is closely related to the nature of the species present on the support after calcination that in turn is greatly influenced by the preparation method, the metal loading and the nature of the support itself.

The goal of this work was to gain more insight into the structure and the electronic properties of Co/Mn/TiO<sub>2</sub> catalytic systems using X-ray absorption spectroscopy at Mn and/or Co K-edges.

Important in this respect was to investigate the influence of the preparation method, and the effect of Mn on the final structure of the catalysts. For this purpose, two series of samples were prepared using two preparation methods: incipient wetness impregnation (IWI), and homogenous deposition precipitation (HDP). Aqueous solutions of Co and Mn nitrates were used to impregnate or to precipitate the metal precursors. Table 1 summarises the details of the catalyst prepared and characterized during this experiment.

**Table1:** summary of the catalysts prepared and measured at Dubble.

<b>Sample code</b>	<b>Co wt %</b>	<b>Mn wt %</b>	<b>Support</b>	<b>Preparation method</b>
IWI-Co	10.5	0	TiO <sub>2</sub>	IWI
IWI-CoMn	10.5	1	TiO <sub>2</sub>	IWI
IWI-MnCo	10.5	1	TiO <sub>2</sub>	IWI
HDP-Co	7.5	0	TiO <sub>2</sub>	HDP
HDP-CoMn	7.5	2	TiO <sub>2</sub>	HDP + IWI
HDP-CoMnT	10	4	TiO <sub>2</sub>	HDP

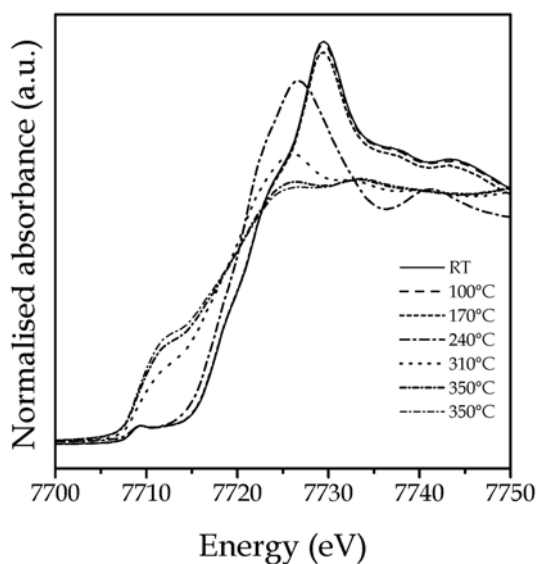
The samples have been studied as self-supporting wafer placed in our in-house controlled atmosphere cell operating at 1 atm that allows full *in situ* treatment. The calcined catalysts have been measured before, during and after reduction in H<sub>2</sub>/He flow at 300 and 350 °C and a subsequent FTS reaction at 200 °C in H<sub>2</sub>/CO flow. The two corresponding gas mixtures used for these reactions were prepared in the experimental hutch from pure gases. In general EXAFS was recorded before and after the treatments whilst short XANES measurements were made during the

same treatments. Due to low Mn loading, the catalysts were measured in fluorescence mode at Mn and/or Co K-edges. All the prepared catalysts could be measured successfully and the data obtained were in general of good quality.

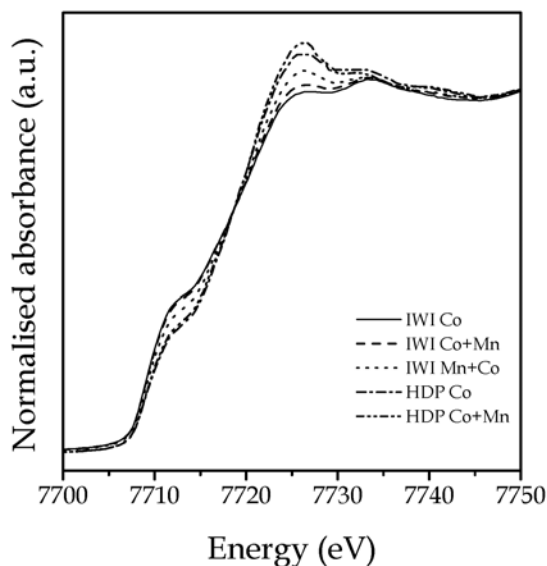
EXAFS data are being currently analysed in order to elucidate the structures of both Co and Mn phases present in the catalysts. However, XANES measurements can already point out the dramatic changes in the local structure and electronic properties experienced by Co and Mn atoms during the reduction treatment.

Figure 1 is a good example of the quality of the data we obtained in this run. It shows the dramatic changes of the XANES spectra measured every 10mn at the Co-K-edge during the heating and the stabilisation stage of the reduction of pure Co titania-supported catalyst prepared by IWI method. The spectrum at room temperature corresponds to  $\text{Co}_3\text{O}_4$ , which is transformed into  $\text{CoO}$  at  $240^\circ\text{C}$  and further reduced to  $\text{Co}^0$  at  $350^\circ\text{C}$ .

Figure 2 that present the XANES spectra of the different catalysts measured after 1 hour of reduction at  $350^\circ\text{C}$ , clearly illustrates the variation of the reducibility of the Co phase according to the preparation method and the Mn loading used. The extent of the oxidation of the Co atoms that can be evaluated by measuring the building up of the maxima of the spectra as well as the shift of the edge towards higher energy is always higher in the samples in which Mn is present as well as in those prepared by the HPD method.



**Fig 1:** Normalised XANES spectra at the Co K-edge during the temperature programmed reduction of pure Co  $\text{TiO}_2$ -supported catalyst prepared by IWI.



**Fig 2:** Comparison of the normalised XANES spectra obtained after 1-hour reduction at  $350^\circ\text{C}$  for the various catalysts investigated.