



	<b>Experiment title:</b> <i>In-situ</i> XAS/DRIFTS/MS study of Cu/Al <sub>2</sub> O <sub>3</sub> catalyts for low temperature SCR of NO <sub>x</sub> with NH <sub>3</sub>	<b>Experiment number:</b> CH 4840
<b>Beamline:</b> BM23	<b>Date of experiment:</b> from: 15/02/2017 to: 20/02/2017	<b>Date of report:</b> 02/03/2017
<b>Shifts:</b> 18	<b>Local contact(s):</b> Manuel MONTE CABALLERO	<i>Received at ESRF:</i>

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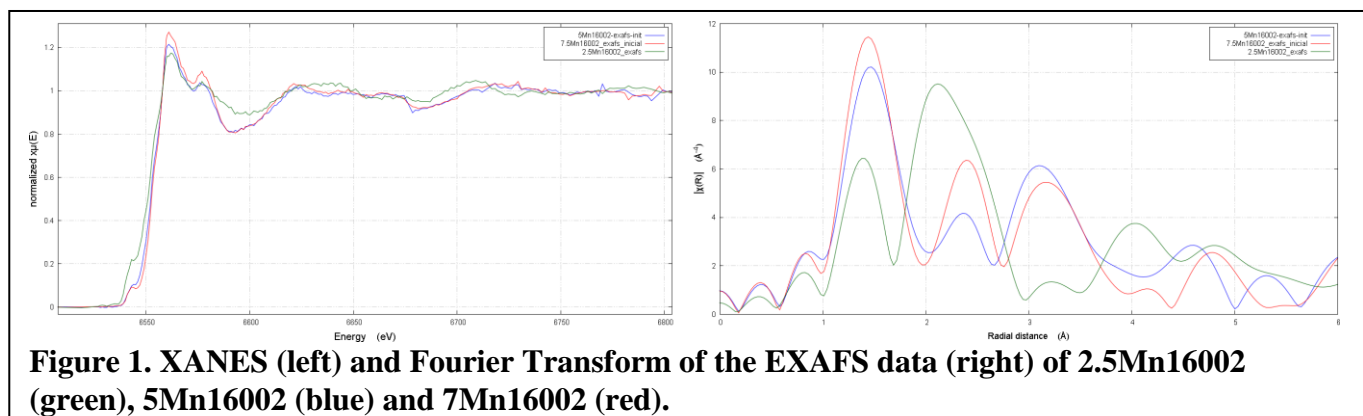
Due to the date of the experiment, just ten days before this report, it must be considered a preliminary one.

Proposal was written for copper system of great interest in the SCR reaction. Unfortunately, a contamination problem was found on the samples prepared for the beamtime; at the time when this happened we didn't have time to go back and synthesize the samples again. In order to leverage the beamtime, we choose to study another system for the same reaction, with the same experimental design and same objectives of analysis. Thus, we employed manganese-based catalyts which energy edge is close in energy with respect to the copper one and which are also of great interest as they are very active at low temperatures. Those catalyts consist on manganese (usually 5%) over mixtures of titanium oxide and sepiolite (sometimes also carbon) prepared with different formulations and by different procedures.

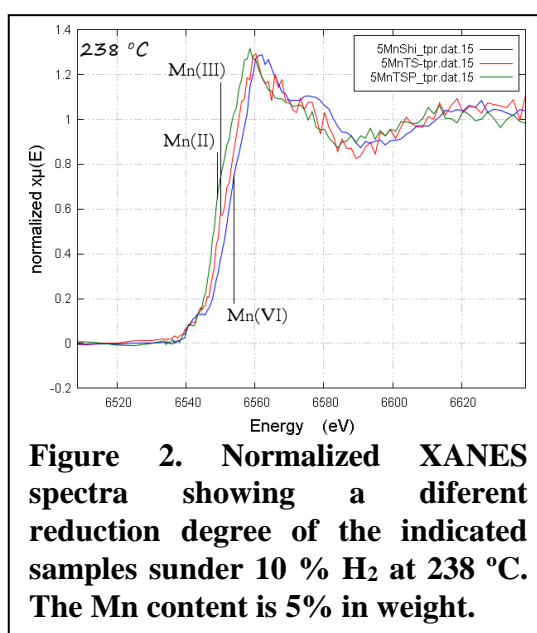
Initial XAS spectra show that in all samples, the manganese was in (VI) oxidation state but, in those with 10% carbon (over a 3:7 sepiolite:TiO<sub>2</sub> mixture) in the support for which it was somewhat between (VI) and (III). All references are characterized by a first shell of oxygen atoms around 1-2 Å and a second shell of manganese atoms around 2-3 Å, with different amounts and mean distances. Samples follow the same scheme.

The support of the most active sample was chosen for an additional trial in which samples with different manganese concentration (2.5, 5 and 7%) were analysed by EXAFS to compare the effect of metal amount in the final particle size (and its relation with the activity). Figure 1 show the XANES (left) and Fourier Transform of the EXAFS data (right). The most active sample (blue), is the one with medium manganese content and a lower intensity of the second shell. This, point to a small particle size of manganese phase and, thus, an increase of the available active centres for the reaction. Lowering the Mn content does not imply a better performance. In this case, is possible

that the manganese interact much more with the support losing its ability to perform the desired reaction.



In order to study the electronic properties a temperature programme reduction, TPR, (70 ml/min of 10% H<sub>2</sub> in He, heating at a rate of 2 °C/min from room temperature to 500 °C, which is the current temperature limit of the DRIFTS cell) was performed *in-situ*, followed by XAS and MS a different behaviour was observed for each sample. As an example, in figure 2 are represented three XANES spectra at 238 °C: while Mn over sepiolite (blue) is still in the initial state; in the others, with 70 % of TiO<sub>2</sub> and with (green) or without (red) 10% of C, the Mn is reduced to (III) or (II). Due to the complexity of the system, a factorial analysis (by a linear combination fitting of all spectra with appropriate patrons) is needed to determine the number nature and evolution of species. Data which will be related, afterwards, with the activity and particle size of each sample in order to obtain a clear picture of the effects induces by the different supports.



Furthermore, an *operando* study was performed over most relevant samples, as current state of the art point to the possibility of these systems to suffer a transformation under the reaction mixture at high temperature (flow of 65 ml/min with 1% of NO<sub>x</sub> and NH<sub>3</sub> and 10% of O<sub>2</sub> in He; heating at a rate of 1 °C/min from room temperature to 300 °C). Which could be an explanation of the different activities of each sample. Whereas, results show that active species remain stable during the whole process.

Additionally, with the objective of understanding the interaction of the manganese phase with the different reactants several experiments were performed combining XANES with DRIFTS spectra and changing the composition of the gas phase: from NO+O<sub>2</sub> to NO+O<sub>2</sub>+NH<sub>3</sub> to NH<sub>3</sub>. Looking for the best conditions, the experiment was performed for three samples at 120 °C, 150 and 200 °C. However, due to technical problems with the DRIFTS spectrometer no useful data could be obtained. In spite of the efforts, the path of the infrared light (source-sample-detector) was not clear and no change in the DRIFTS spectra was detected even after rising NH<sub>3</sub> to 1% at 2 bar inside the cell; when its bands are more easily detected in the lab (with a different set-up).