EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

	Experiment title: Operando combined XANES/XRD investigation of Bi and Pb migration in the promoted iron catalysts for selective light olefin synthesis from syngas	**Experiment number:** CH-5569
Beamline: BM26A	**Date of experiment:** from: 21/09/2018 to: 25/09/2018	**Date of report:** 13/12/2018
Shifts: 12	**Local contact(s):** Dipanjan Banerjee	*Received at ESRF:*

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Report:

1. Results and the conclusions of the study

In situ synchrotron techniques such as X-ray absorption fine structure spectroscopy (XAFS) have been shown to be very useful to study active phases in their working environment. XAFS can be divided in two spectral regions, the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) provide detailed information about the oxidation state and coordination of the absorber atoms. In situ XAFS can be employed as a bulk characterization technique to identify and quantify the different iron oxide and carbide species present during FTS at relevant working conditions.

Here, we did in-situ XANES experiments to study the evolution of the Bi promoter phase under realistic conditions of Fischer-Tropsch synthesis. Figure 1 shows the in-situ study of Bi L_{III}-edge XANES spectra. The Bismuth presents oxide states in the fresh FeBi/CNT catalyst, the Bi oxide is gradually reduced to metallic phase during treatment in CO at 350 ºC (Figure 1a). Interestingly, the metallic Bi re-oxidized to oxidation state after cooling down to room temperature in CO which can be explaied by Bi facilitating oxygen scavenging in the surface iron carbide and thus then formation of Bi oxide. However, no reoxidation occured in the mechanical mixture Fe+Bi catalyst and we can say that the Bi promoter which located in the surface of iron can helps the dissociation of CO. Interestingly, small amount of metallic Bi re-oxidized to oxide state over the used Fe+Bi mixture catalyst during cooling down in CO, this can be explained by migration of Bi to the surface of iron carbide.

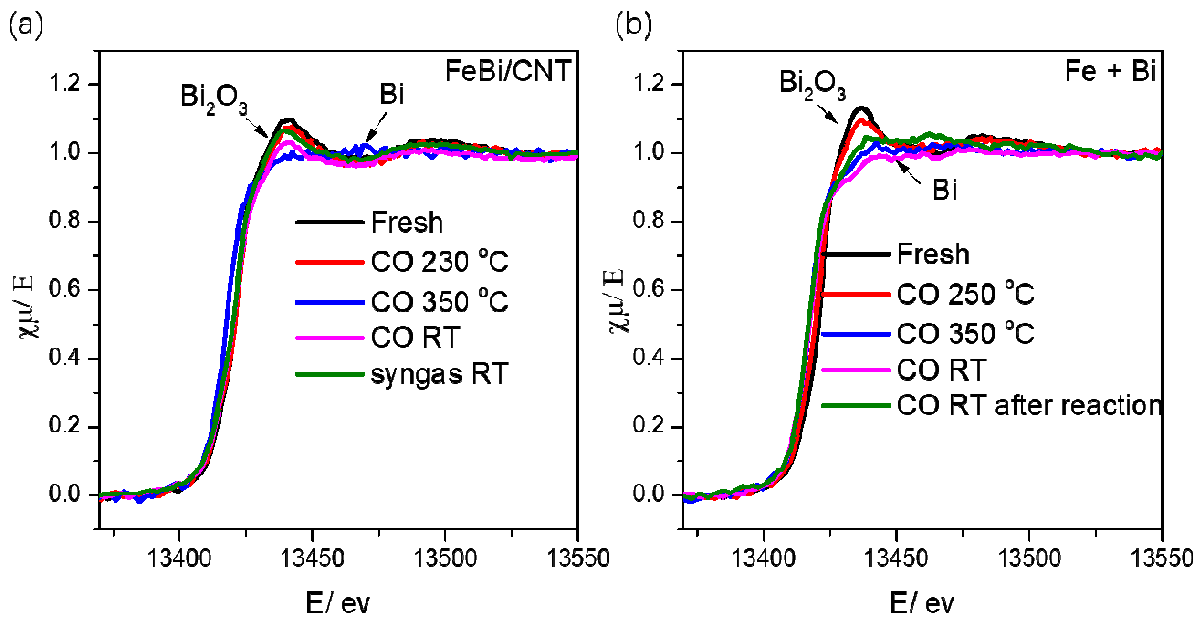

Figure 1. In-situ Bi L_{III}-edge XANES spectra. (a) FeBi/CNT, (b) Fe/CNT + Bi/CNT mixture.

The use of in situ and ex situ characterization techniques provide strong evidence for potential promotion mechanisms in the Bi and Pb promoted iron-based catalysts. It is clear that re-oxidation of metallic Bi is taking place at the employed FTS operating conditions. It can conclued that the promoters, which are located at the interface of iron carbide particles, facilitate CO dissociation by scavenging O atoms.

2. Justification and comments about the use of beam time

The in-situ XAS experiments were perfomed uisng optmized beamnline and setup. Dipan helped us a lot to improve the resolution and taught us how to use the setup more efficientlly. The experimental set-up in BM26A beamline is very useful, we did a lot of in-situ experiments without exposure with air. The experiment can be performed under high pressure better understanding of the active metal and promoters phase evolution during the activation and reaction was acheived. The design of the set-up is very good and its easy to increase or decrease the treatment temperature and pressure accurately. The alignmenet and resolution of the beamline were also very nice and its easy to change the positon and intensity according with your samples.

3. Publication(s):

- Confinement of iron and promoters in carbon nanotubes for direct selective synthesis of lower olefins from syngas over Bi and Pb promoted iron catalysts (in progress, will be submitted early 2019).

- Operando XAFS/XPS characterization of FeBi catalysts: Bi redox cycle and migration (in progress, will be submitted early 2019).