



	Experiment title: Rh-Cs interactions in Fisher-Tropsch Catalysis: an in-situ XAS-MS study	Experiment number: CH-3805
Beamline: Id24	Date of experiment: from: 12/12/2013 to: 18/12/2013	Date of report: 20/02/2015
Shifts: 18	Local contact(s): Sakura Pascarelli	<i>Received at ESRF:</i>
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Report:

The Ru-Cs supported on high surface area graphite systems using chloride precursors appear to be a good option for Fisher-Tropsch (F-T) reaction. Studies in our lab demonstrate that alkali promotion improves remarkably the selectivity to light olefins, diminished the production of methane and increase higher molecular weight hydrocarbons (C5-C12) product yields.

Within the 18 shifts allocated to this proposal we were to mount, and carried out combined experiments using mass spectrometry and X-ray absorption at the Ru K-edge and Cs-L-edge, cycling gas reaction mixtures, for the *in situ* time-resolved study of the active/promoter components response under “real” operation conditions. These experiments have yielded crucial information that has allowed us to unveil: **i)** the mechanism of interaction between the two components (originated during the reduction) and **ii)** mechanistic details of the Ru and Ru-Cs performance.

In particular, we have analysed the oxidation state changes (XANES Ru K-edge) during a reduction pre-treatment by using statistical factor analysis of the spectra during reduction pre-treatment. The analysis shows that Cs alters Ru activation during H₂ treatment; a new intermediate phase is detected due to the interaction between both metals that conduct to final bigger particle size and an alloy formation (Fig.1.)

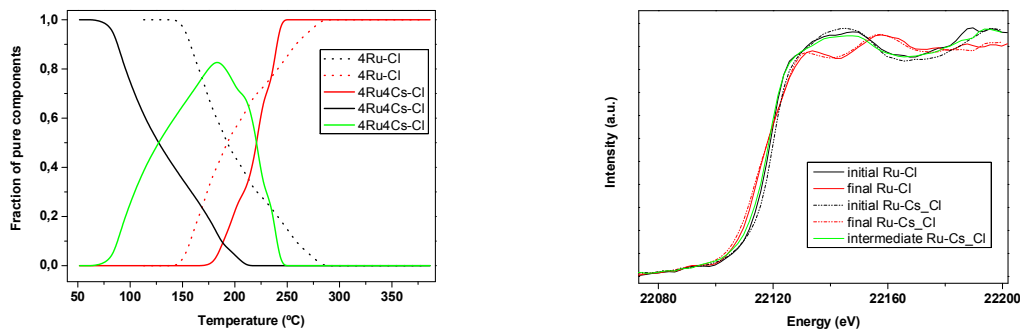


Fig1. Ru species and their evolution during temperature H₂ pre-treatment for 4%Ru/C and 4%Ru-4%Cs/C samples.

This alloy modifies the catalytic response of Ru entities during Fisher-Tropsch reaction: time resolved EXAFS (Ru K-edge) through a step change between both reactants (CO/H₂) at the reaction temperatures evidenced changes with the creation and evolution and/or concomitant disappearance of several metal-atom bonds formed upon contact with the different gas atmospheres, what has kinetic implications. After the removal of H₂, we can link noble metal morphological changes to surface contact with CO; contact with CO triggers a flattening of the particle evidenced by evolution of the second Ru-Ru coordination shell and the almost unalterable numbers of the others. Fig.2. shows this morphological influence of CO/H₂ interaction with Ru.

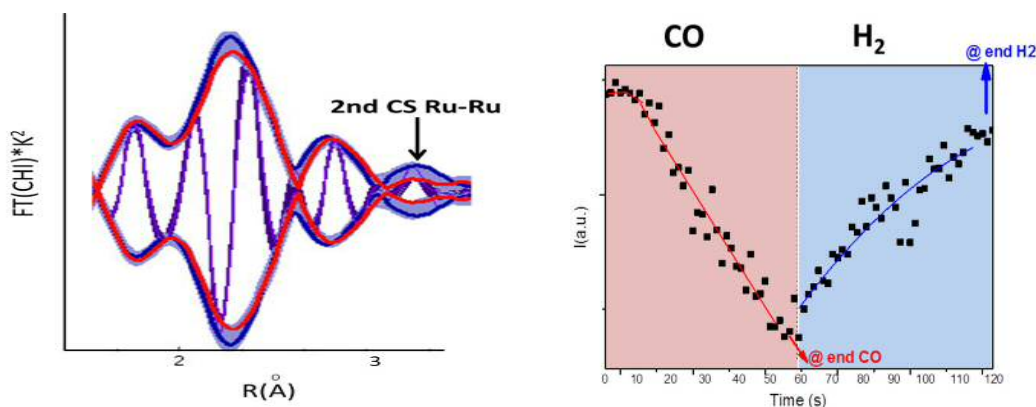


Fig.2 a) Fourier Transform during CO-H₂ cycling changes b) temporal evolution of the Ru-Ru 2nd coordination layer.

In alkali presence, this strong CO interaction with Ru, (also observed by calorimetry experiments in the lab) conducts to longer retention times of the carbonaceous fragments (showed by synchronous MS) which favour the production of longer chain hydrocarbons.

Unfortunately due to technical issues, the measures at the Cs L3 edge did not have adequate quality for analysis. Later experiments performed September 2014 at ALBA synchrotron allowed to complete and confirm the conclusions that have been exposed.

As noted above, these results provides information on the **structural/electronic changes which go from the precursor (under H₂) to the “active” (under reaction) states** and are expected to contribute to the understanding of a relevant chemical process in the production of hydrocarbon from biomass

Finally, we would like to thank Dr G. Agostinni and S. Pascarelli for the extensive support they have given during this experiment.