



	Experiment title: Coupled <i>in situ</i> XAS and IR study for elucidation of the role of Ru promotion and TiO ₂ polymorph on the catalytic activity of CoRu/TiO ₂ catalysts for Fischer-Tropsch synthesis	Experiment number: CH-4839
Beamline: BM23	Date of experiment: from: 22-02-17 to: 28-02-17	Date of report: 28/02/17
Shifts: 18	Local contact(s): Dr. Debora Meira	<i>Received at ESRF:</i>
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Abstract

In our current research, we have noted remarkable differences in activity and selectivity for Ru-promoted Co/TiO₂ catalysts in Fischer-Tropsch synthesis (FTS) depending on the TiO₂ crystalline phase (A-anatase, R-rutile) and Ru content on anatase-based catalysts, which we can hardly explain exclusively using conventional characterizations (e.g. XRD, H₂-TPR, CO-IR, XPS, etc.). Interestingly, we observed notable changes in the Co₃O₄ → CoO → Co⁰ reduction kinetics for the A- and R-supported Co-Ru catalysts, suggesting a different functioning of Ru (location, Ru-Co interaction, etc.) as cobalt reduction promoter depending on the TiO₂ polymorph carrier and Ru loading. Different Co reduction kinetics may translate into different types of surface Co⁰ sites after H₂ reduction which will ultimately impact the catalytic performance. The aim of this study was to perform coupled *in situ* XAS and IR synchrotron studies on our catalysts at different stages: calcined, during H₂ reduction at different temperatures (220-400°C), and during FTS under realistic (220°C, 10 bar) conditions as an insightful approach to explain our results. Such information will enable us to derive solid structure-reactivity correlations that are of paramount importance for designing improved Co-based FTS catalysts with clear practical implications.

Experimental details

Four reduced and passivated powder samples have been studied under different reaction conditions using the XAS+IR cell available on BM23 beamline. Ru K-edge XAS measurements were performed in fluorescence mode using a EXAFS setup with a scanning Si (311) double crystal monochromator. The time resolution of the spectra (1 to 5s per point)

reported herein varied depending on Ru loading on samples ($k_{\max}=12$) and on average three scans were acquired to improve the signal-to-noise level of the data for fluorescence measurements. XAS data processing was performed using IFEFFIT with the Horae package (Athena). Spectra acquisition has been performed at different steps of activation and reaction and a high quality EXAFS spectra have been collected in the following conditions: 1) at 25 °C under H₂ flow; 2) spectra acquisition at 100 °C under H₂ flow after reduction; 3) spectra acquisition at 220 °C after 3 hours of FTS reaction under *syngas* flow. All spectra were collected under ambient pressure. Unfortunately, the Co K-edge has not been measured due to complex and time-consuming analysis on Ru K-edge (fluorescence mode, Ru loading on samples, etc).

Results

The normalized XANES spectra of reduced CoRu/TiO₂ catalysts after reduction are represented in Figure 1a. It is possible to observe that after reduction the absorption edge for all samples is positioned at 22117 eV (same position of Ru foil), characteristic of Ru in oxidation state 0. However, even the Ru being in the metallic state, the oscillations beyond the edge suggest different local environment of Ru in CoRu/TiO₂ samples compared to Ru bulk (dash dot). Moreover, the EXAFS oscillations on samples with lower Ru loading (0.2 and 0.4 wt%) are different relative to samples with higher content (arrows in Figure 1b), giving evidences that Ru neighborhood is different on these samples (Figure 1b). For more reliable interpretation of the system, we plan to investigate Co K-edge to follow Co reduction kinetic and obtain complementary information to Ru K-edge in order to elucidate the active phase.

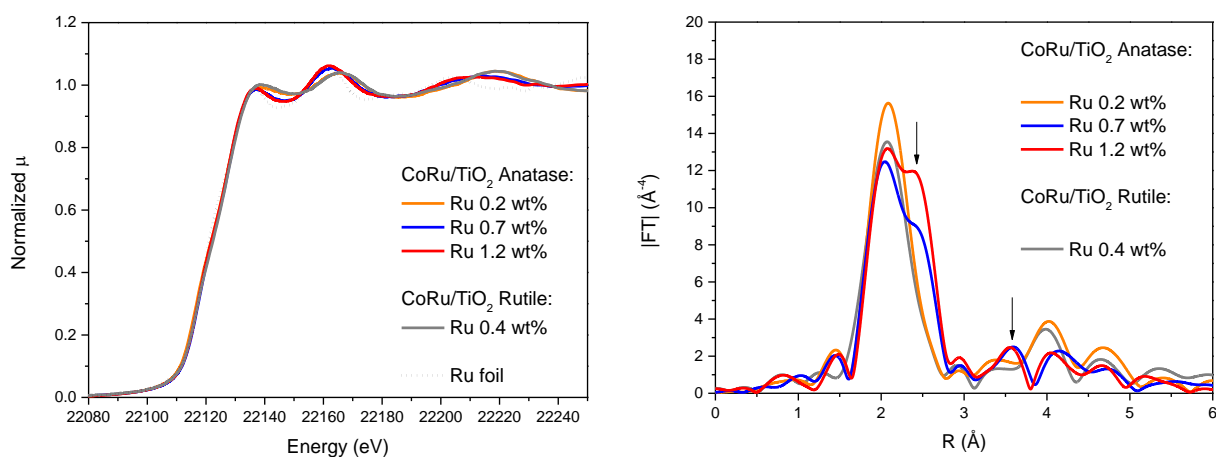


Figure 1. Ru K-edge normalized XANES (a) and $|FT|$ spectra of reduced CoRu/TiO₂ studied catalysts.

Conclusions and future work

The results obtained from the XAS analysis will be combined with laboratory techniques performed in our home institute. These results will be very important since the materials have shown different catalytic results in FTS reactions. At the moment we need time for spectra interpretation and their correlation with infrared measurements. We kindly thanks ESRF the opportunity to perform our investigation in their facility and also the beamline scientist (Debora Meira) for her help and also the possibility to use the XAS+IR catalytic cell of the beamline. Also, we plan to apply for beamtime another in next run to follow the Co reduction kinetics that, unfortunately, was not possible to be performed on this run.