

Report on beam time: CH3214, BM29

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In-Co-Ferrierite Catalysts for Natural Gas Vehicles; a multitechnique synchronous XAS/DRIFTS/MS study.

Within the 18 shifts allocated to this proposal we were to mount and carried out X-ray absorption experiments using a new plug-flow reactor designed and constructed by Drs. S.J.A. Figueroa and M.A. Newton. Synchronous, multitechnique experiments using XAS as one of the technique are only possible (due to transmittance problems of our samples) at ID24, and will be run in the second part of this experiment (June, 2010). The main objective using BM29 was carrying out in-situ Quick-XAS (XANES and EXAFS) experiments at both Co and In K-edge under operando conditions. The latter corresponds to the first Quick-XAS experiment run at BM29 using a Si(311) monochromator.

In-Co-ferrierite catalytic systems have been shown to be highly active and stable under real operation conditions (e.g. in the elimination of methane and NO_x in lean conditions and presence of steam, CO₂, and S-contamination) and require the establishment of an adequate structure-activity relationship under operando conditions in order to explore its potential for industrial application [1,2]. Our XAS experiments are aimed to answer this question by comparing such bimetallic formation with another supported on ZSM-5 and the corresponding Co and/or In Ferrierite-based monometallic references, which always displays significantly poorer catalytic performance.

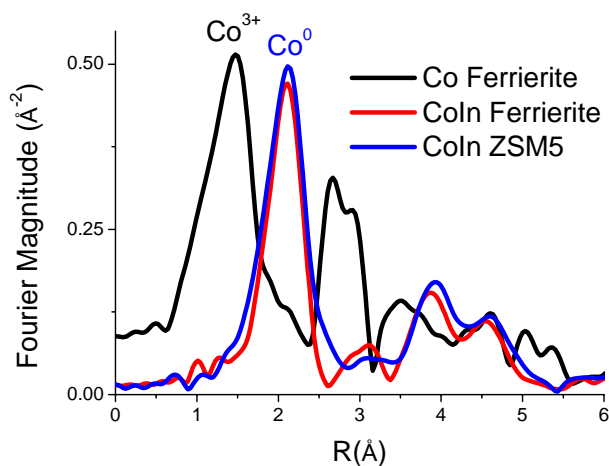
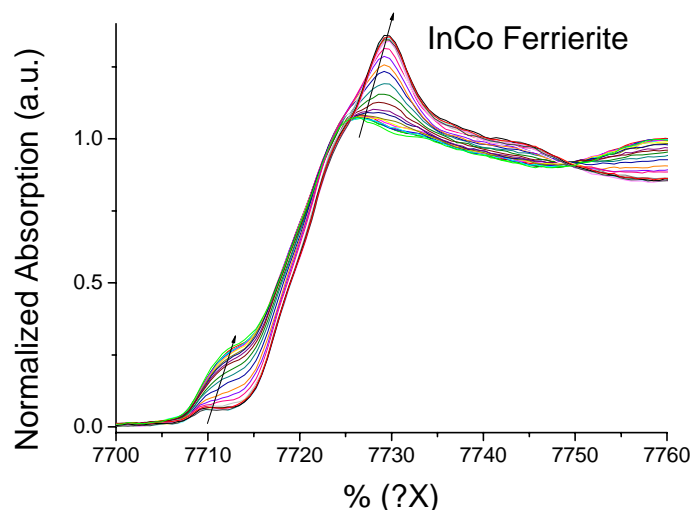


Figure 1. Co K-edge XAS spectra of several catalysts; upper panel, EXAFS Fourier Transform of catalysts initial state; lower panel; XANES spectra of In-Co-Ferrierite taken during a reaction run (RT \rightarrow 500 °C; 6 °C/min). See text for details.



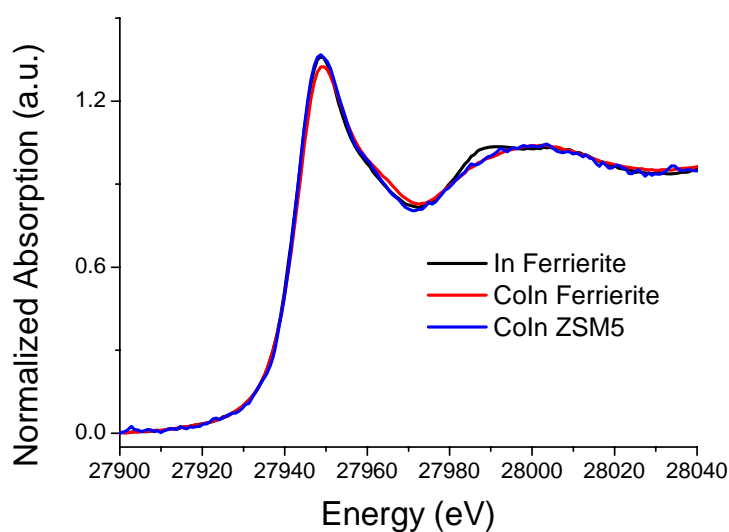
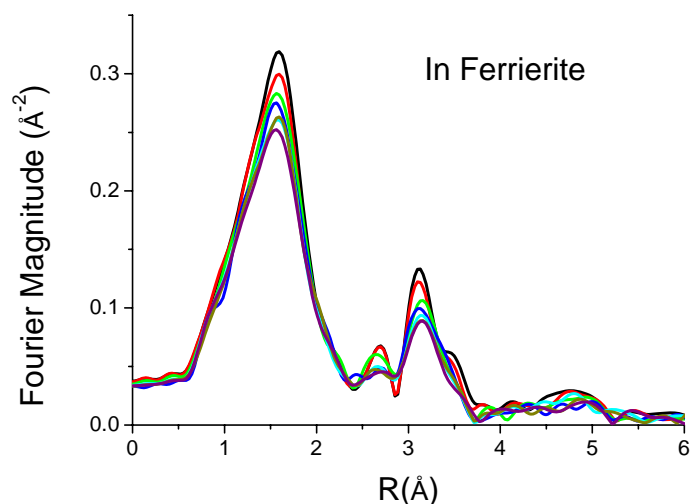


Figure 2. In K-edge XAS spectra of several catalysts; upper panel, initial XANES of catalysts initial state; lower panel; EXAFS spectra of In-Ferrierite taken during a reaction run (RT \rightarrow 500 $^{\circ}$ C; 6 $^{\circ}$ C/min). See text for details.



So, as a first step, experiments at both edges (Co K-edge, Fig. 1; In K-edge, Fig. 2) were carried out during a light-off test (RT to 500 $^{\circ}$ C) under a typical, lean (0.2%) CH_4 + (0.1%) NO + (3 %) O_2 gas mixture at a SGHV of ca. 50.000 h^{-1} . Co K-edge data showed that bimetallic catalysts have an initial metallic state while the ferrierite-based monometallic reference has a Co^{3+} state (Fig. 1). The metallic state is a consequence of the preparation method as the bimetallic preparation procedure ends with a He treatment at 673 K in order to achieve the adequate activation of In [1,2]. No differences were observed at the In K-edge initial state (Fig. 2). Moreover, during the light-off ramp, the only single change observed appeared at the Co K-edge of bimetallic samples. Such samples suffer an oxidation process as illustrated in Fig. 1, without visible influence of the support (Ferrierite or ZSM-5). Contrarily to Co, the In chemical state is stable; as depicted in Fig. 2 absence of changes other than thermal effects was noticed in both XANES and EXAFS. Thus, it appears that bimetallic systems only suffer an oxidation process of Co during light-off experiments irrespective of the zeolite used as support and, consequently, XAS was not able to uncover any physical differences among samples which may justify activity differences.

Additional isothermal experiments in the 300-500 $^{\circ}$ C interval were also carried out in order to allow physical understanding of the catalytic activity. Co K-edge was unaffected while In modifies its chemical state in response to the presence or absence of oxidant agents in the gas mixture. This provided conclusive evidence of the direct involvement of In at the slow reaction step of the process and the redox-type mechanism of the reaction. The time-resolution of the experiments (1 min. in the case of In K-edge) was enough to study the reduction behaviour in absence of oxidants while the oxidation was essentially completed within a single spectrum. An example of the In reduction process is given in Fig. 3 for the monometallic In-ferrierite system.

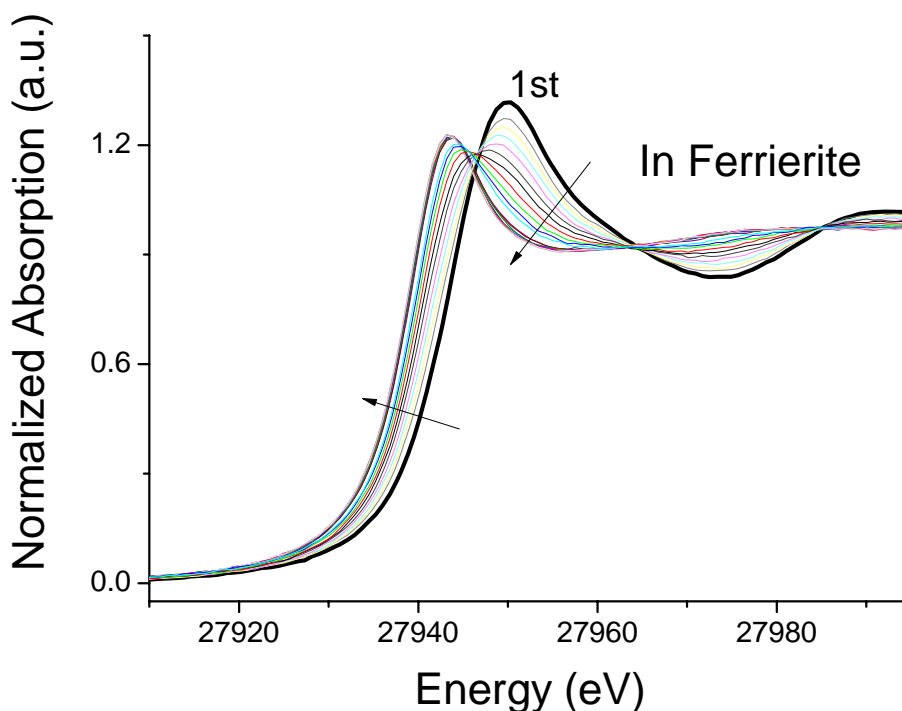


Figure 3. In-Ferrierite XANES spectra taken during a isothermal run at 300 °C starting with the full mixture (1st spectrum), following by a CH₄ (in He) treatment.

In all samples In reduction is slow, indicating, as mentioned, that the slow reaction step is related to the In contact with the hydrocarbon species. The thermal behaviour of this process is different for the corresponding catalysts, with onset differences of ca. 75 °C between the CoIn-Ferrierite system and the other two studied (In-ferrierite and CoIn-ZSM-5). This appears to justify the activity differences among samples and quantitative analysis of the activation energy of this process (four temperatures for each catalyst) is currently underway using Factor Analysis techniques to measure the temporal variation of In chemical states during reduction. The presence of isosbestic points and the shape of the initial/final spectra (Fig. 3) would indicate the presence of two species in all cases; the initial species is an In(III) species in a rather specific configuration (typically called InO⁺ in the literature) while the final species appears to be In(I). EXAFS changes during isothermal events are rather complex but the process seems completely reversible (in terms of redox state and size) and would thus suggest the limited influence of morphology changes in the present results. The run finished with an analysis of the effect of adding water (2.5 % H₂O) to the gas stream during the isothermal events. A preliminary, visual analysis indicates that thermal effects are softened in presence of such molecule and thus a lower activation energy could be obtained in this case with respect to a dry gas mixture. We plan to complete the study using ID24 to obtain XANES (EXAFS is not possible) during both reduction and oxidation isothermal steps with a higher temporal resolution (ca. 0.5 s).

So, as a summary of the report, we believe the present study was able to uncover the mechanism and slow reaction step of the systems and adds valuable information concerning the physical-variables driving to active systems, useful in the context of exhaust gas purification of natural gas vehicles. The active CoIn bimetallic system appears to have an improved interaction and activation of the hydrocarbon through a redox-type mechanism, being this the slow rate step of the reaction. It appears the active phase with Co possibly affecting the redox behaviour of such element by indirect ways (according to EXAFS preliminary analysis), mostly related with the In-phase particle size.

Finally, we would like to thank Dr S.J.A. Figueroa for the extensive support he has given this experiment. Without his support and know-how it could not have been the success that it has turned out to be.

References

- 1.- A. Kubacka, J. Janas, E. Wloch, B. Sulikoski, *Catal. Today* 101 (2005) 139.
- 2.- A. Kubacka, J. Janas, B. Sulikoski, *Appl. Catal. B* 69 (2006) 43.