


Experiment title:

In-situ QEXAFS of the reactivity of bimetallic PtPd supported catalysts towards H₂S : support effect and thioresistance.

Experiment number:

SI 1106

Beamline:	Date of experiment: from: 29/09/04 to: 05/10/04	Date of report: 15/01/05 <i>Received at ESRF:</i>
Shifts:	Local contact(s): Y. Soldo	

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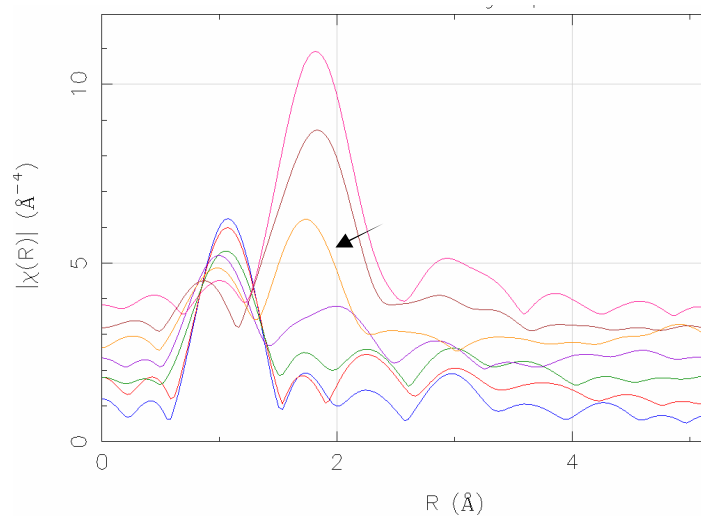
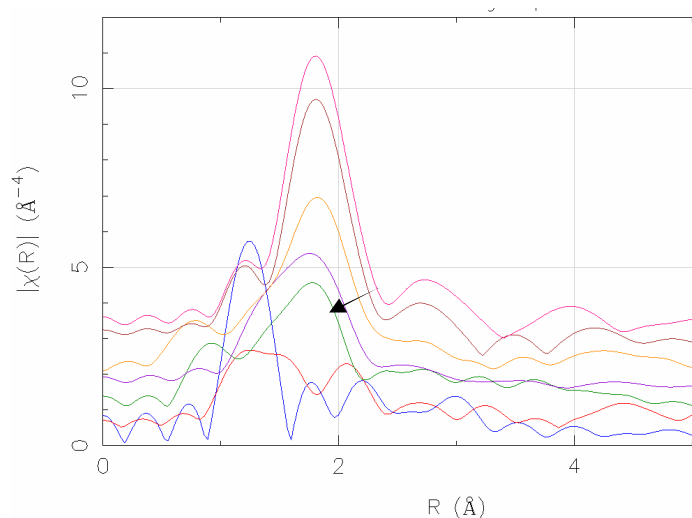
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Report:

Unfortunately the fluorescence detector required for the experiment was not available (the Canberra detector was expected to be back from the factory in GB after reparation). So, we had to modify our scheduled experiment and had to work in transmission mode. Two main studies were performed.

Activation of CoMo on alumina catalysts impregnated with triethyleneglycol.

We studied the activation of hydrotreating catalysts (CoMo on alumina) at both Co K-edge and Mo K-edge. We followed by QEXAFS the activation (transformation of the oxidic state into a sulfided state) under in-situ condions. the objective of the experiment was to compare the kinetic of sulfidation of a CoMo catalysts unpromoted and promoted with an organic compound : the triethyleneglycol TEG). The presence of such additive on the catalyst in the oxidic state enhances the catalytic performances. the origin of this promoting effect is not yet clarified and subject to many assumptions. One of them concerns the fact that the organic compound delays the sulfidation of the active phases and allows the formation of more active systems by this way. In the present study, we attempted by QXAS to follow during in situ sulfidation of CoMo on alumina catalysts containing various contents of TEG and a non promoted catalyst. The fist figures reflects this transformation during which Mo-O bonds are transformed into Mo-S bonds i.e. a contribution at higher distance in the FT. For the reference catalysts this nex contribution is clearly seen in the green curve corresponding to a temperature treatment of 140°C (series of FT on the left, arrow), by contrats with the TEG treated catalyst Mo-S contribution appears only à 200°C (yellow FT on the right, arrow).



a) FT at Mo K edge during sulfidation of a CoMo on alumina reference catalysts .

b) FT at Mo K edge during sulfidation of a CoMo on alumina catalysts promoted with TEG.

A similar effect was obtained at Co K edge, indicating that the sulfidation of both elements is slowed down due to the presence of TEG.

Mo and Nb site occupancy in the $\text{Nb}_2\text{Mo}_3\text{O}_{14}$ oxide .

As recently established, mixed oxide $\text{Mo}_3\text{Nb}_2\text{O}_{14}$ has the Mo_5O_{14} – type structure eminently important for catalysis (Fig1). This compound, which can be considered as a generic host for the mixed oxide catalysts, demonstrates an original property of being partially auto-reduced independently on the preparation conditions. To explain this unusual finding, substitutional disorder between Nb and Mo was suggested which induce instability of O15 atom to the second order Jan Teller distortion and further internal redox rearrangement. The closeness of Nb and Mo masses prevents from determination of occupational distribution between Nb and Mo. EXAFS is the only technique able to provide information on the site occupancy in this system. As clearly demonstrates comparison of the EXAFS spectra, Nb and Mo in this solid have different coordination (Fig2).

Double edge fit reveals a strong tendency of Nb to occupy pentagonal bipyramids, whereas molybdenum has preference for distorted octahedral, containing abundant double bonds. Distinguishing the preferential occupation of sites by Nb and Mo is crucial for the understanding of this newly observed phenomenon of the mixed oxide structurally –induced auto-reduction.

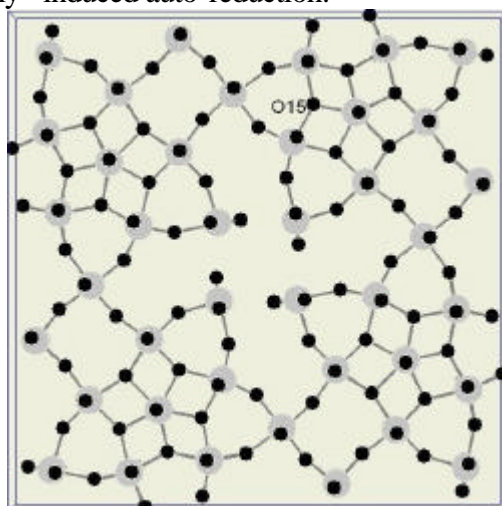


Fig.1 Mo_5O_{14} structure with the O15 atom marked

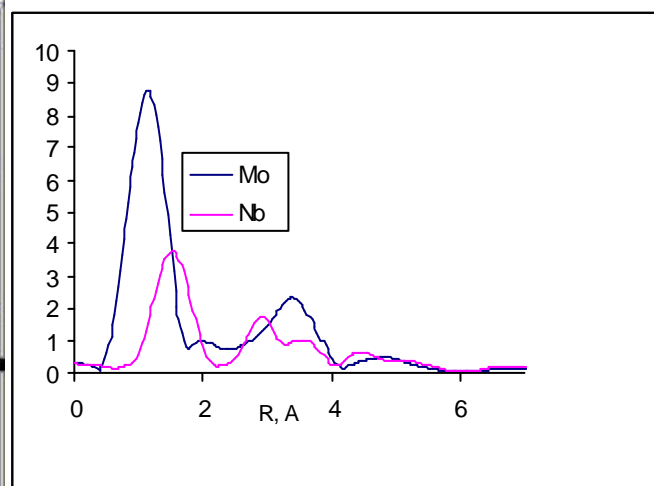


Fig.2. FT module of Nb and Mo K edge spectra