

## In situ XAFS of Ru<sup>0</sup> and RuS<sub>2</sub> supported on HYd or Al-SBA-15

Juliette BLANCHARD<sup>1</sup>, Kyoko K. BANDO<sup>2</sup>, Takashi MATSUI<sup>2</sup>, Masaru HARADA<sup>2</sup>, Michèle Breyse<sup>1</sup> and Yuji YOSHIMURA<sup>2</sup>

<sup>1</sup>Laboratoire de Réactivité de Surface UMR CNRS 7609, Université Paris VI, 75252 Paris, France

<sup>2</sup>National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan

### Introduction

Ruthenium sulfide supported on dealuminated acidic Y zeolites (HYd) are among the most active catalysts for the hydrogenation of aromatics in presence of sulfur. However, the nature of the active site is fully understood yet. *In situ* XAFS studies during the formation of the active phase by reductive sulfidation under 15% H<sub>2</sub>S/H<sub>2</sub> till 673 K and under reaction conditions (lower partial pressure of sulfur, and presence of aromatic in the feed, T=523 K) could improve our understanding of these systems. The *in situ* XAFS cell we used in this study is the one successfully developed and used in the course of a previous proposal [2].

### Experimental

[Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>] was ion-exchanged in the porosity of the zeolite a dealuminated Y zeolite (Ru loading 1.5 wt%). A wafer of dried sample catalyst (200 mg, 10 mm in diameter) was set in a newly developed in-situ XAFS cell [1]. The sample was sulfided under 15% H<sub>2</sub>S/H<sub>2</sub> (flow rate: 100 ml/min) by increasing the temperature up to 673K by successive steps of 50K and maintaining the temperature at 673K during 1.5h. After this pretreatment, the temperature was set at 523 K and the composition of the gas flowing through the reactor was gradually changed (the amount of H<sub>2</sub>S was decreased to 2%, 350 ppm). Eventually toluene was introduced by a pump (feed rate 0.01 ml.min<sup>-1</sup> of liquid toluene). Ru K-edge XAFS spectra were measured at BL10B. All the spectra were observed by a step-scanning mode with a data accumulation time of 0.5 – 1 sec for each step. Analysis of the data was conducted with commercially available software (REX, Rigaku Co.). Parameters for curve-fitting analysis were extracted from spectra observed of standard substances at the reaction temperature.

### Results and Discussion

Sulfidation occurs readily as testified by the immediate shift in the position of the first neighbors peak and is complete at 373 K where N<sub>S</sub>=5.7 (that is close to 6 the maximal value). Reduction of RuS<sub>2</sub> starts at 423 K and continues till 573 K with the appearing and growing of a peak corresponding to Ru-Ru scattering (d<sub>Ru-Ru</sub>=2.6 Å), and the decrease in the intensity of the peak corresponding to Ru-S scattering (d<sub>S</sub>=2.2 Å), indicating that surface desulfidation and reduction occur simultaneously. The composition of the Ru first shell after reduction at 573 K is N<sub>S</sub>=3.7 and N<sub>Ru</sub>=3.2, indicating a strong desulfidation of the catalyst and the formation of Ru<sup>0</sup> domains.

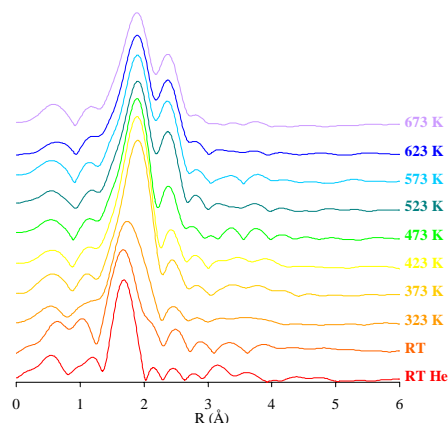


Fig.1 Fourier transform of Ru K-edge EXAFS ( $k^3\chi(k)$ ) spectra observed upon increasing temperature during the reductive sulfidation of Ru/HYd.

The temperature of the cell was then decreased to 523 K and the partial pressure of H<sub>2</sub>S was gradually decreased. However even after 3h under 2% H<sub>2</sub>S/H<sub>2</sub> + 3h under 350 ppm H<sub>2</sub>S/H<sub>2</sub>, the spectra remained unmodified, indicating that the system did not undergo important desulfidation at this time scale. This result, which is in contradiction with previous reports, might indicate that desulfidation occurs at a longer time scale. The spectra is however significantly modified upon introduction of toluene in the feed as can be seen on fig 2. The main change is a decrease in the intensity of the Ru-Ru scattering peak, that, upon fitting seems to be exclusively due to an increase in the Debye Waller factor, that could indicate a disorganisation of the structure upon toluene chemisorption on the metallic sites.

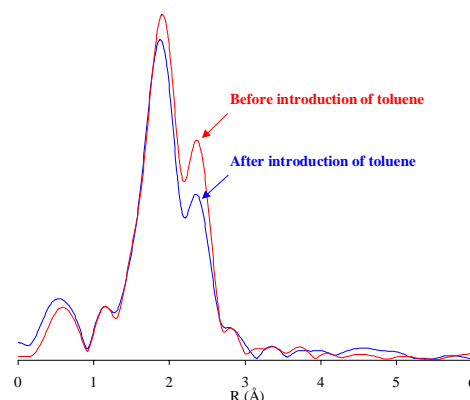


Fig.2 Fourier transform of Ru K-edge EXAFS ( $k^3\chi(k)$ ) spectra of RuS<sub>x</sub>/HYd observed before and after introduction of toluene.

### References

[1] K. K. Bando, et al., J. Sync. Rad. , 8, 581 (2001).

[2] Proposal No. 2002G274

\* jblanch@ccr.jussieu.fr