



	Experiment title: Testing of a novel tool for studying working catalysts under real reaction conditions.	Experiment number: CH-1785
Beamline: ID24	Date(s) of experiment: From: 14-DEC-04 To: 20-DEC-04	Date of report: 15/3/2005
Shifts: 18	Local contact(s): Dr. Mark A. Newton	
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Report :

During this experimental time we were able to test a new setup for obtaining combined *in situ* ED-EXAFS, UV-Vis and Raman spectroscopy in order to study heterogeneous catalysts under real working conditions. To our best knowledge, this is the first in-situ device which couples three spectroscopic techniques in one reactor which focuses on the same spot of a metal oxide catalyst under true reaction conditions and is capable of delivering sub second time resolution (since all techniques obtain their information in a dispersive mode probing all energies simultaneously). However for these experiments the acquisition times used were 400 ms for EDXAFS data, 1 s for Raman, 2 s for the UV-Vis and 10 s for the mass spectrometer. However due to the time delay for read out from the Princeton detector and the need to shutter the Raman laser in order to avoid saturation of the UV-Vis signal the time resolution between each acquisition was reduced to approximately 4-5 s for the EDXAFS, 10 s per UV-Vis and 15 s per Raman spectra. A schematic of the setup is given in figure 1.

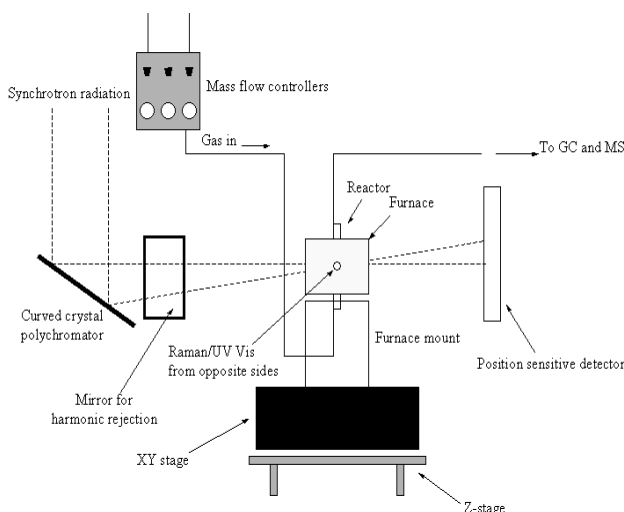


Figure 1. Schematic of the multitechnique setup used on ID24.

In order to test this setup we carried out a series of studies using 13 wt% Mo/Al₂O₃ and 13 wt% Mo/SiO₂ incipient wetness impregnated catalysts during successive reduction (5% H₂ or C₃H₈ in Helium)/oxidation (5% O₂ in Helium) cycles at 550°C. Since the three techniques are sensitive to changes in the molybdenum oxidation/coordination states it was possible to obtain complementary information on the catalysts behaviour and therefore the set-up allows us to discriminate between the dynamics of both catalysts under reaction conditions, as well as to identify the active site and the deactivation pathways.

Propane dehydrogenation over a 13 wt% Mo/SiO₂ catalyst.

In Figure 2 we show data collected using the three techniques in tandem during the first propane dehydrogenation cycle for the 13 wt% Mo/SiO₂ catalyst. The initial features observed in the spectra included a distinct 1s-4d pre-edge feature at 20001.5 eV in the Mo K-edge ED-XANES, a strong LMCT band at 470 nm in the UV-Vis and bands in the Raman spectra at 992, 820 and 664 cm⁻¹ which are consistent with the presence of Mo⁶⁺ species on the catalyst surface in a mixture of tetrahedral/distorted octahedra environments. These features quickly diminished during the subsequent propane dehydrogenation step and in particular the bands corresponding to the MoO₃ phase as well as a band at 1350 cm⁻¹ (due to the BN internal standard) had disappeared after only 10 mins. This corresponded with a levelling off of the UV-Vis spectra. The changes in the ED-XANES data which included a decline in pre-edge peak intensity, an increase in the 1s-5p transition feature at 20021.7 eV as well as a shift in the position of the white line from 20010.9 to 20010.1 eV which continued until the reaction ceased some 20 minutes later, was consistent with a reduction of some of the Mo⁶⁺ to Mo⁴⁺. However the changes observed in the Raman and UV-Vis data are also associated with the formation of coke on the catalyst.

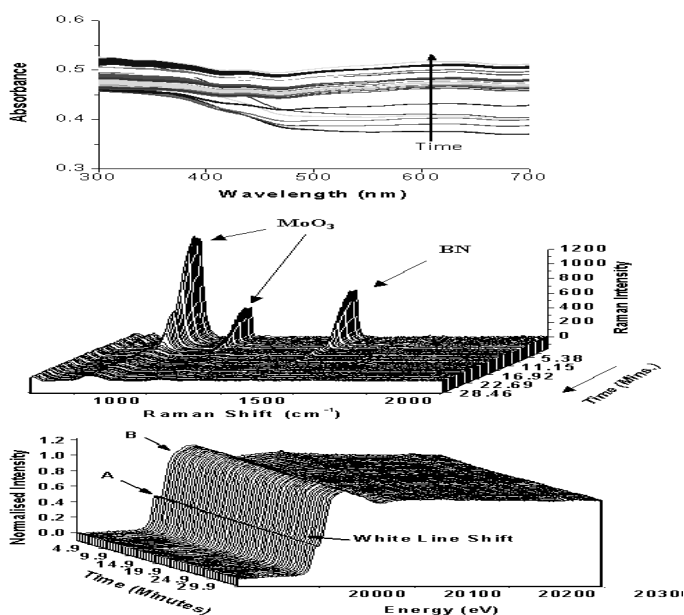


Figure 2. UV-Vis (top), Raman (middle) and ED-XANES (bottom) data acquired during the 1st propane dehydrogenation cycle for the 13 wt% Mo/SiO₂ catalyst. Note that features A and B in the ED-XANES data correspond to the 1s-4d and 1s-5p transition at the Mo K-edge respectively.

We were able to repeat these measurements twice more (after oxidative regeneration) and found that due to changes in the catalyst local structure the performance differed. Furthermore we also studied the behaviour of the corresponding 13 wt% Mo/Al₂O₃ material and compare its catalytic performance under the same conditions and (along with the Mo/SiO₂ material) during reduction treatment with 5% H₂ in Helium. An early analysis of the results suggested that there were differences in redox behaviour between the two types of catalysts but critically this combination of techniques is able to show why this is so. Further data analysis is currently in progress.