

Coupled XAS-Raman *Operando* analysis of TiO₂ supported oxomolybdate catalysts in methanol conversion

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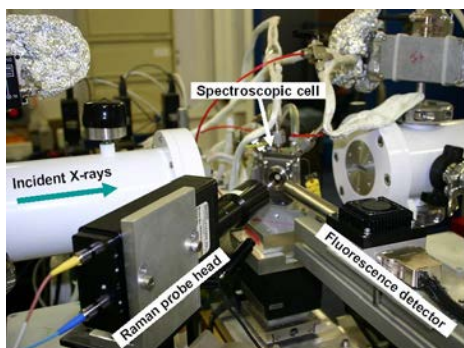


Figure 1. *Operando* Raman-XAS coupling setup.

INTRODUCTION

Although heterogeneous catalysts are essential in numerous chemical processes, the exact structure of the active phase remains unsolved in many cases. In order to understand the structure-reactivity relationships, a relevant approach consists in examining the catalyst while operating. This so-called *operando* approach has recently attracted a fast growing attention and was applied to various spectroscopic techniques: IR, Raman, Electron Paramagnetic Resonance (EPR), UV-visible and X-ray Absorption Spectroscopy (XAS). However, it generally appears that one single spectroscopic technique does not make it possible to spell out the complexity of the catalytic process. Therefore, the direct coupling of complementary *in situ* or *operando* techniques offers a multiple and simultaneous characterization of a working catalyst for a much better understanding of the catalytic process. Such studies request the use of a single spectroscopic reactor fitting the

combined peculiarities of catalysis and the involved spectroscopic techniques. The coupling of XAS and Raman spectroscopy was successfully performed in a commercially available *operando* chamber to supplement our previous Raman studies on TiO₂ supported oxomolybdate catalysts.¹ The investigated selective oxidation of methanol is both a major economic reaction for vaporization of biomass by-products and a probe reaction broadly used to study redox and acido-basic properties of bulk and supported oxides.

EXPERIMENTAL

The catalysts were prepared by incipient wetness impregnation of an ammonium heptamolybdate solution on pure anatase TiO₂ commercially available by Sachtleben™. The specific area of the support was 93.5 m².g⁻¹ after a pre-treatment (rinse with distilled water and calcination 5h at 500°C). The concentration of the impregnation solution was adjusted in order to reach a molybdenum

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loading corresponding to 7.5%_{wt} MoO₃/TiO₂.

Catalyst *in situ* and *operando* characterization by combined XAS and Raman spectroscopies was performed at the French Synchrotron Radiation Facility SOLEIL on the SAMBA beamline. X-ray Absorption Near Edge Structure (XANES) spectra were recorded at the Mo K-edge (20000 eV) using a Si(220) sagittally focusing double crystal monochromator. The monochromatic beam was focused at the sample position onto a spot of 200 × 300 μm² and the fluorescence signal was recorded by a Silicon drift detector. Using a fast scan of the step by step monochromator, only 4 minutes were needed to collect one XANES spectrum (19900-20200 eV). Therefore, a rather good monitoring of the catalyst was allowed in working conditions at different temperatures and under selected atmospheres.

The *in situ* and *operando* analyses were allowed by using an [environmental spectroscopic chamber](#) developed by Harrick with a special planar dome designed for Raman measurements¹. The silica window was replaced by a thin mica plate (200 μm thick) to improve its transmission towards X-rays without any dramatic alteration of the Raman signal.

Due to its implementation on the beamline, the spectroscopic cell was vertically set up and oriented at 45° with respect to X-rays incident beam and fluorescence detector^{2,3}, as shown in Figure 1. The gas flow through the powdered catalyst was reversed compared to usual operation in order to help maintaining the powder inside the sample holder in vertical position. The methanol was introduced in the spectroscopic chamber by means of a He flow bubbling in a saturator equipped with a condenser whose temperature was set to 0°C to get a methanol partial pressure of 3.91 kPa.

Simultaneously to XANES data, Raman spectra were recorded in working conditions using a Kaiser HL5R Raman spectrometer. A Raman probe head equipped with a long working distance objective (×10) facing the sample was used to focus the 514.5 nm excitation beam and collect the scattered light (Figure 1). Optical fibres were used for light guiding and the scattered light was collected by an air-cooled CCD.

RESULTS AND DISCUSSION

The 7.5%_{wt} MoO₃/TiO₂ catalyst was first activated by a gradual increase in temperature

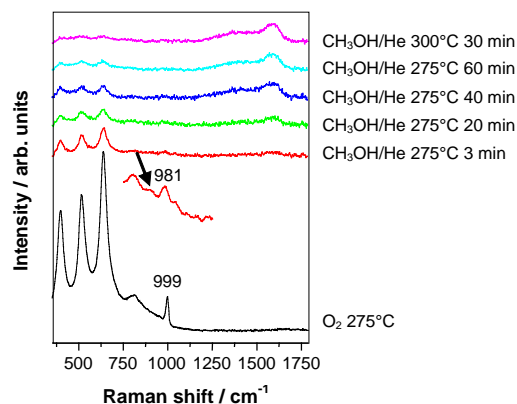


Figure 2. Raman spectra evolution along *operando* experiment.

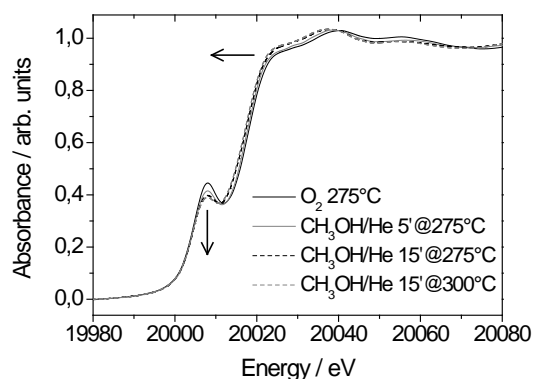


Figure 3. Evolution of the XANES spectra along *operando* experiment.



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(5°C.min⁻¹) up to 350°C under pure oxygen flow. The structural evolution of the active phase was then examined while flowing CH₃OH/He at 275°C. No oxygen was introduced in the feed to allow the characterization of the reduced species although a CH₃OH/O₂/He mixture is generally used for a continuous regeneration of the active phase along the catalytic process.

The *operando* Raman and XANES spectra recorded under CH₃OH/He flow at 275°C are reported in Figures 2 and 3. The Raman spectrum of the activated catalyst (Figure 2, black curve) exhibits three lines at 396, 513 and 618 cm⁻¹ characteristic of well crystallized anatase, and a sharp line at 999 cm⁻¹ assigned to terminal Mo=O stretch vibration, $\nu(\text{Mo}=\text{O}_t)$. Upon CH₃OH/He flow, the intensity of the Raman spectrum rapidly and markedly decreases. The $\nu(\text{Mo}=\text{O}_t)$ mode is still detected (981 cm⁻¹) after 3 minutes of exposure, which is not the case anymore after 20 minutes on stream. In parallel, broad lines are detected around 1300 and 1600 cm⁻¹ indicating surface poisoning by heavy carbon species in absence of oxygen. On the contrary, the 2800-2950 cm⁻¹ range remains blank, indicating that the methanol and product fragments do not last durably at the surface of the

active phase.

Changes along exposure to CH₃OH/He flow were also pointed out on the XANES profiles (Figure 3). The intensity of the pre-edge feature is rapidly and noticeably affected. Moreover, a visible shift of the absorption edge to lower energies is observed after 15 minutes at 275°C, which is relevantly amplified upon increasing the temperature to 300°C. The shape of the near-edge spectrum is obviously modified, suggesting a true change in the coordination of the molybdenum with a partial reduction of the molybdenum active sites under methanol flow⁴.

Both spectroscopic techniques are indicative of rapid structural evolutions during the catalytic process and give complementary information. These results confirm the relevancy of this time-resolved, coupled *operando* analysis of catalysts. A comparison with other catalysts of different structures (e.g. TiO₂ supported oxomolybdate catalysts with a low molybdenum loading) should allow going one step further in the understanding of the structure-reactivity connections.

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