Methanol conversion over TiO$_2$ supported oxomolybdate catalysts. An *In Situ* Raman spectroscopic study

**INTRODUCTION**

The catalytic selective oxidation of methanol is a fine way to afford valuable products such as dimethoxymethane (DMM), methylformate (MF) or formaldehyde.

In addition, as methanol conversion involves oxidation and dehydration/condensation reactions, the reaction itself is a very relevant way to investigate both redox and acidic properties of a catalyst\(^1\). Raman spectroscopy makes it possible to analyze the structure of the active phase with a short collection time and suitable spatial resolution. Moreover, in some favorable cases, the nature of adsorbates, intermediates or poisons can also be observed.

Time and space resolution make Raman spectroscopy a technique of choice in the *operando* and *in situ* study of the catalyst under working conditions.\(^2,3\)

**EXPERIMENTAL**

The catalysts were prepared by wetness impregnation of an ammonium heptamolybdate solution on a commercially available anatase provided by Sachtleben™ which specific area is fixed to 50 m\(^2\)/g by the purchaser. The concentration of the impregnation solution was adjusted in order to reach a molybdenum loading corresponding to 5\% _w_ MoO$_3$/TiO$_2$.

Micro-Raman spectra were recorded in working conditions at different temperatures and under selected atmospheres using the 531.95 nm second harmonic line of a Nd:YAG laser. A 50X microscope objective was used to focus the excitation beam (13.6 µm spot) and collect the scattered light at the same time. The scattered light was collected through a confocal hole (150 µm) by a nitrogen cooled CCD (Labram Infinity, Jobin Yvon).

The *in situ* analysis was allowed by using an environmental spectroscopic chamber developed by Harrick equipped with a new planar dome including a pure silica window to permit Raman measurements in the UV-visible range.

The methanol was introduced in the spectroscopic cell by means of a He flow bubbling in a saturator equipped with a condenser which temperature is set to 11°C.

**RESULTS AND DISCUSSION**

The 5\% _w_ MoO$_3$/TiO$_2$ catalyst was activated in the environmental spectroscopic cell by a 3 hours heat treatment under pure oxygen flow at 350°C. This step has been reported to enhance dehydration and activation of the redox sites. The blue line in Figure 2 is the Raman spectrum of the activated material under pure O$_2$ flow without contact to air after activation treatment.
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The influence of the reactive mixture on the structure of the active phase has been explored by *in situ* Raman spectroscopy directly performed on the activated catalysis. The Raman spectra recorded upon heating in pure MeOH/He flow are presented in Figure 2.

Exposure to pure methanol carried by helium led to significant changes in the Raman features of the active phase: The intensity of the line observed at 950 cm$^{-1}$ vanishes gradually with increasing temperature. This trend, already observed in other catalytic systems was connected to effective reduction of Mo$^{VI}$ to Mo$^{V}$ 4. This supports the reasonable methanol conversion (15% at 240°C) to MF (yield: 5%) and formaldehyde (yield: 10%) observed for this catalyst in plug flow reactor (feed: MeOH/O$_2$). Introduction of oxygen in the reactive mixture led to reverse spectral changes so about half the initial intensity of the Raman peak at 955 cm$^{-1}$ is recovered (not shown).

Insights on the nature of adsorbates formed upon methanol flow can be afforded by Raman spectroscopy as well. Thus, the *in situ* Raman spectra presented in Figure 3, peaks at 2855 and 2957 cm$^{-1}$ and respectively assigned to the symmetric and antisymmetric stretching modes of CH$_3$ are observed together with new features at 1444 and 1577 cm$^{-1}$ upon pure MeOH/He flow (Figure 3a). These last bands are not observed any more when introducing oxygen in the feed whereas CH$_3$ stretching vibrations are still detected upon MeOH/O$_2$ flow. Assignment of the lines detected around 1500 cm$^{-1}$ is not straightforward, however, based on previous studies 4, the latter can be due to COO vibration in formate adsorbed intermediates. Introduction of O$_2$ in the reactive mixture (Figure 3b) led to a complete loss of the presumed formate vibration bands, indeed, the remaining line observed around 1660 cm$^{-1}$ is a harmonic mode of anatase. This could support a van Krevelen - type mechanism, involving adsorption of methanol on the oxomolybdate phase, and subsequent release of the oxidation reaction products. Interestingly, the CH$_3$ stretching modes are still observed, with a clear doubling which is not yet completely elucidated. Upon pure oxygen flow, all the adsorbates are removed from the catalyst’s surface.

**REFERENCES**