

Methanol conversion over TiO_2 supported oxomolybdate catalysts. An *In Situ* Raman spectroscopic study

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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 catalyst¹. 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

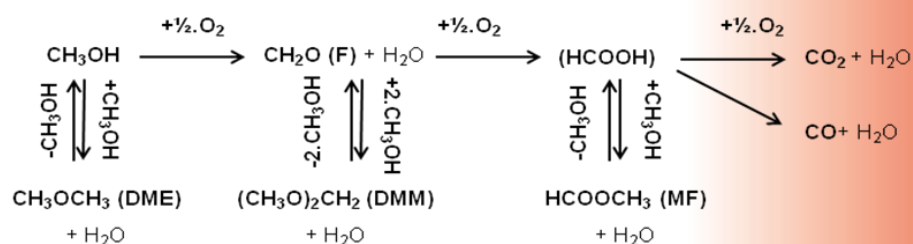


Figure 1. Oxidation of Methanol.

Sachtleben™ which specific area is fixed to 50m²/g by the purchaser. The concentration of the impregnation solution was adjusted in order to reach a molybdenum loading corresponding to 5%_{wt} MoO₃/TiO₂.

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%_{wt} MoO₃/TiO₂ 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 O₂ flow without contact to air after activation treatment.

applications note

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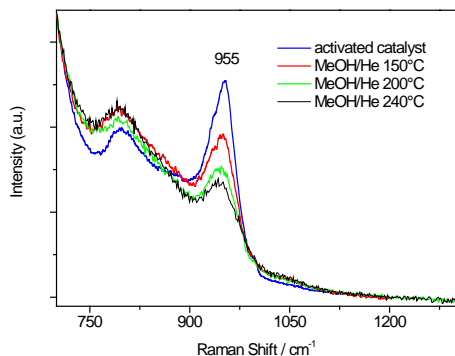


Figure 2. *In situ* Raman spectra of the supported 5% MoO₃ catalyst upon MeOH/He flow.

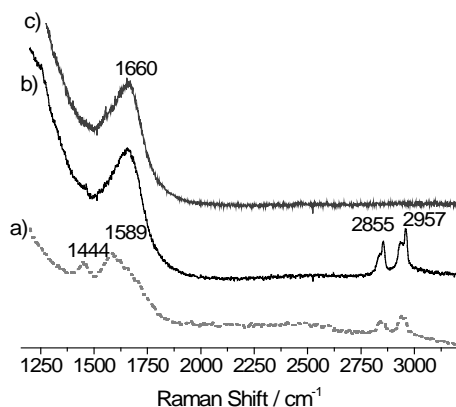


Figure 3. *In situ* Raman spectra recorded at 240°C upon a) pure MeOH/He flow b) mix MeOH/O₂ c) pure O₂.

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^V⁴. 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/O₂). 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 CH₃ 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 CH₃ stretching vibrations are still detected upon MeOH/O₂ flow. Assignment of the lines detected around 1500 cm⁻¹ is not straightforward, however, based on previous studies⁴, the latter can be due to COO vibration in formate adsorbed intermediates. Introduction of O₂ 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 CH₃ 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.

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