Methanol conversion over TiO₂ 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 catalyst. 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.

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 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.
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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$^{V}$. 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, 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**