# REPORT for the experiment # 30–02–772 carried out between the 13th and the 18th of September 2006.

Introduction

Analysis techniques such as XPS and HREELS are generally used to characterize the surface state of heterogeneous catalysts but they cannot be used under working conditions. Infrared and Raman vibrational spectroscopy represent an attractive alternative as they can be applied to probe the catalyst under reaction or Operando conditions. The oxidation state of active sites can also be characterized using bulk analysis techniques such as EPR and XAS to obtain data on an atomic scale. Molybdenum oxide based catalysts are used industrially for the partial oxidation of hydrocarbons such as methanol. The partial oxidation of methanol is of great interest for industrial applications[i] but is also a probe reaction to test the catalytic properties of new preparations. Indeed, numerous studies have shown that methanol oxidation is very sensitive to the nature of active sites and can be used to study the acidic and oxidation properties of catalytic surfaces[ii,iii,iv]. The possible pathways for the reaction of methanol on a bulk or supported metal oxide catalyst are summarized in Scheme 1.
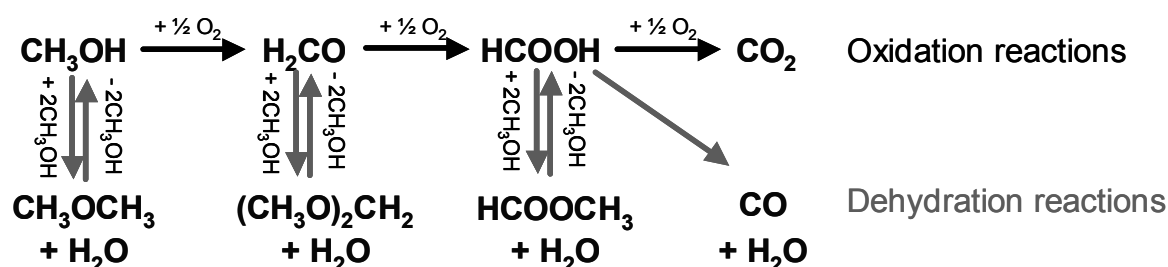
Scheme 1: Reaction pathways in methanol transformation on MoO$_3$ catalysts.

The oxidative-reductive processes lead to oxidized species such as formaldehyde (F), formic acid (FA) and carbon oxides (CO$_x$) whereas acid-base functions mainly lead to the dehydration product (dimethylether - DME). Successive dehydrations of oxidation products can yield dimethoxymethane (DMM) or methyl formate (MF). Hence, the distribution of the reaction products gives indications on the functionalities present on the catalyst surface. Moreover, oxidation of methanol is well adapted for spectroscopic studies[v,vi] and has been described on various materials[vii,viii].

We have focused the present study on the characterization of the active phase and adsorbed species during the oxidation reaction of methanol on a well-designed polymolybdate deposited on titanium dioxide (anatase).

The beam time on the BM30B beam line (experiment # 30-02-772) was dedicated to the observation of the active phase and adsorbed species through the molybdenum probe.

Identification of species during the catalyst preparation

Mo/TiO$_2$ catalysts were prepared by incipient wetness impregnation of titanium dioxide with ammonium heptamolybdate solution (Mo$_7$O$_{26}$(NH$_4$)$_5$,4H$_2$O; HMA) the amount of added HMA being adjusted for the preparation of catalysts with 1 and 5%wt.of MoO$_3$.
After drying overnight at 100°C, the catalysts were calcined in air at 500°C for 3H with a ramp rate of 40°C/h. Samples of 1 and 5%wt.MoO$_3$/TiO$_2$ were taken for each step of their synthesis.

Unfortunately we couldn't collect spectra for the 1%wt. MoO$_3$/TiO$_2$ because the absorption jump was too small (sample not enough concentrated). A proposal for a study using in fluorescence mode has been submitted.
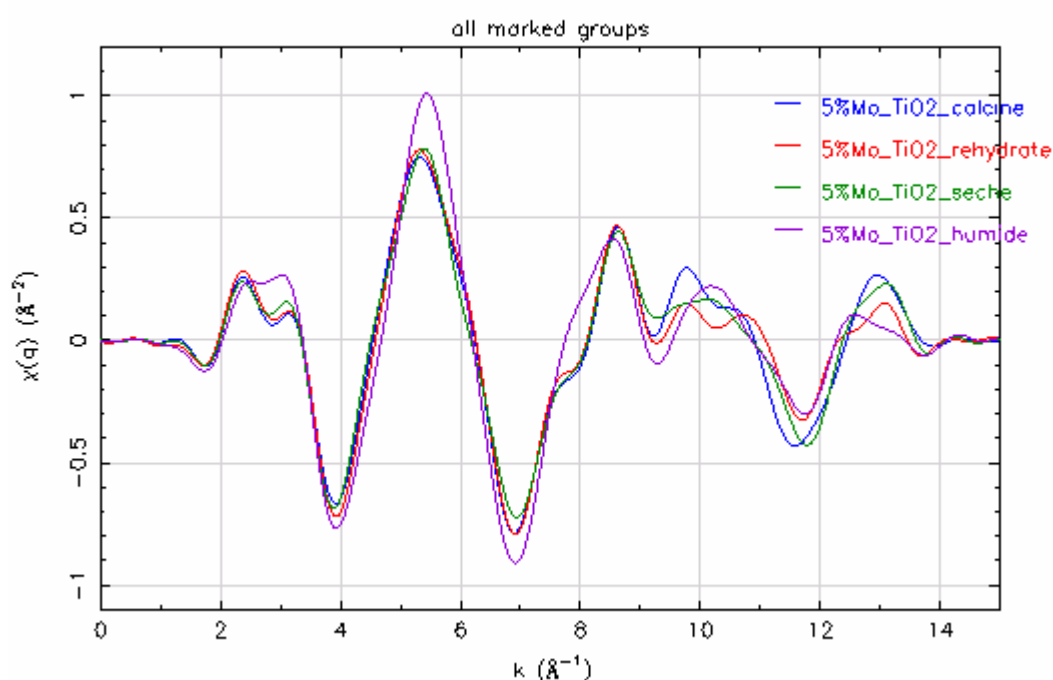

Figure 1: EXAFS spectra at Mo K-edge for 5%wt.MoO$_3$/TiO$_2$ wet, rehydrated, dried and calcined.

On figure 1, we can observe that the spectra of the samples calcined, rehydrated and dried are quite similar; only the spectrum of the wet sample is slightly different. We tried to compare it with other spectra of different compounds: α-Mo$_8$O$_{26}$, the solution of HMA used for the impregnation of titanium and the same solution at pH=2.8 that is assumed to contain the Mo$_8$O$_{26}^{4-}$ entity.

It can be seen on figure 2 that the spectrum of the impregnation solution is very similar to the one of the Mo$_8$O$_{26}^{4-}$. On the other hand, these solutions exhibit spectra that are different from the solid state α-(NH$_4$)$_4$Mo$_8$O$_{26}$. Hence going from a liquid to a solid sample does induce significant changes in the EXAFS spectra. Whether these come from real structural changes or only from structural disorder and slight modifications of bond distances induce by the liquid phase needs to be addressed by simulation of the spectra and modeling of the liquid

phase. The spectrum of the wet sample does not match with the one of the impregnation solution nor with solid α-(NH$_4$)$_4$Mo$_8$O$_{26}$ or MoO$_3$ (not shown). Hence the identification of the species appearing during the different steps of the preparation requires a more in-depth analysis.
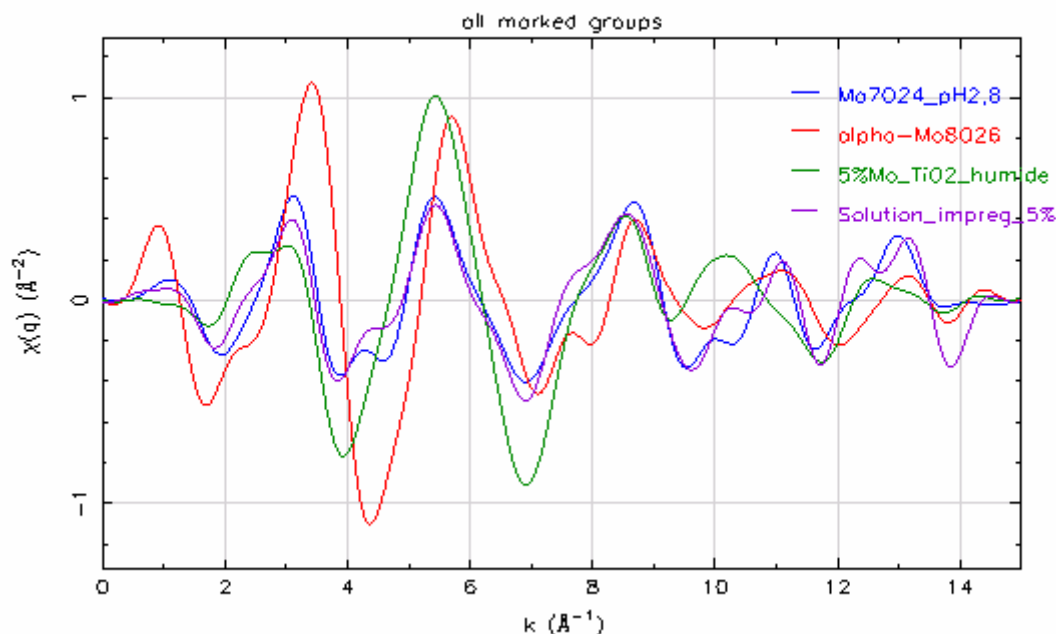

Figure 2: EXAFS spectra at Mo K-edge for 5%wt.MoO$_3$/TiO$_2$ wet, solution of impregnation, α-Mo$_8$O$_{26}$, solution of impregnation at pH=2,8.

Operando study with 5%wt. MoO$_3$/TiO$_2$

Experimental part:

The gas flow is adjusted (He and O$_2$) using mass flow controllers. The flow passes by a saturator filled with methanol at room temperature. A condenser connected to a cooling system adjusts the quantity of methanol. The temperature of the gas is measured with a thermocouple at the top of the condenser. The gas passed then by an Operando home-made cell containing the sample. The sample was first activated in O$_2$ (30cc/min) at 310°C then the test was carried out using a condenser temperature of 11°C with a flow of 16cc/min of He, 10cc/min of O$_2$ and 4cc/min of MeOH leading of a gas composition of about 53% He, 33% O$_2$, 13% MeOH. The Operando test is then carried out at different temperatures. The effluent products were monitored with a Quick gas chromatograph (μ-GC, SRA).

Results:

Figure 3 shows that the pre-edge (19990eV) is more intense after activation in O$_2$ that shows a change of the local geometry of molybdenum that apparently becomes more tetrahedral. This is consistent with a dehydration of the surface molybdenum species. The EXAFS spectra of the catalyst at different moments of the test are shown on figure 4: the

differences between the spectrum of the calcined sample and the activated one indicate a slight structural change of the adsorbed molybdenum species during the activation step.

The structure of the active phase changes slightly after activation under a He/O$_2$/MeOH mixture but there is no effect of the reaction temperature: EXAFS spectra are similar at 295°C and 200°C when we introduce O$_2$ in the gas feed. At these temperatures, the products formed are respectively formaldehyde, methylformate and methylal,
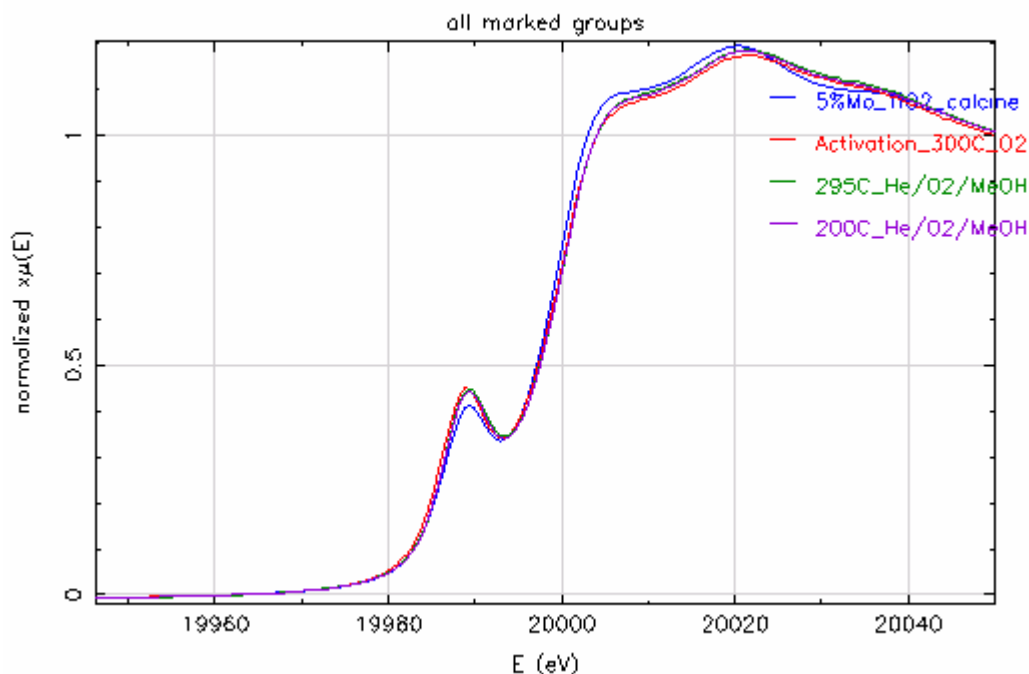

Figure 3: XANES spectra at Mo K-edge: 5%wt. MoO$_3$/TiO$_2$ calcined, sample activated at 300°C in O$_2$, sample at 295°C in He/O$_2$/MeOH and sample at 200°C in He/O$_2$/MeOH.

Figure 4: EXAFS spectra at Mo K-edge: 5%wt. MoO$_3$/TiO$_2$ calcined, sample activated at 300°C in O$_2$, sample at 295°C in He/O$_2$/MeOH and sample at 200°C in He/O$_2$/MeOH.
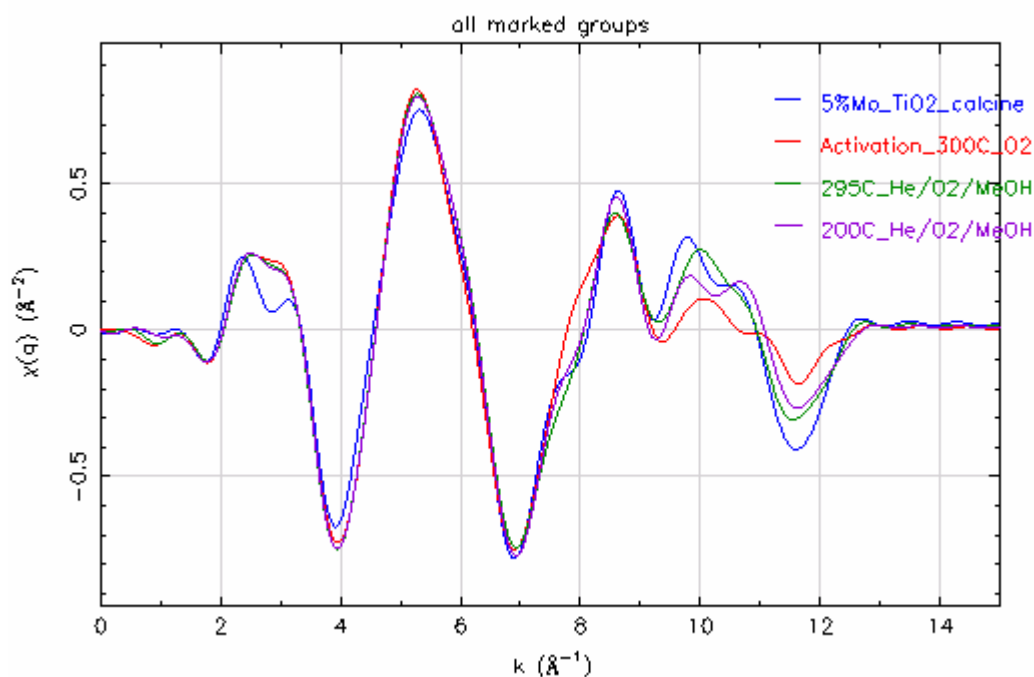
Reduction and re-oxidation 5%wt.MoO₃/TiO₂

If oxygen is removed from the gas feed, the molybdenum phase is reduced by the methanol and there is no possible reoxidation. Hence such experiments are a good way to characterize intermediates molybdenum species as they are trapped in a reduced state.
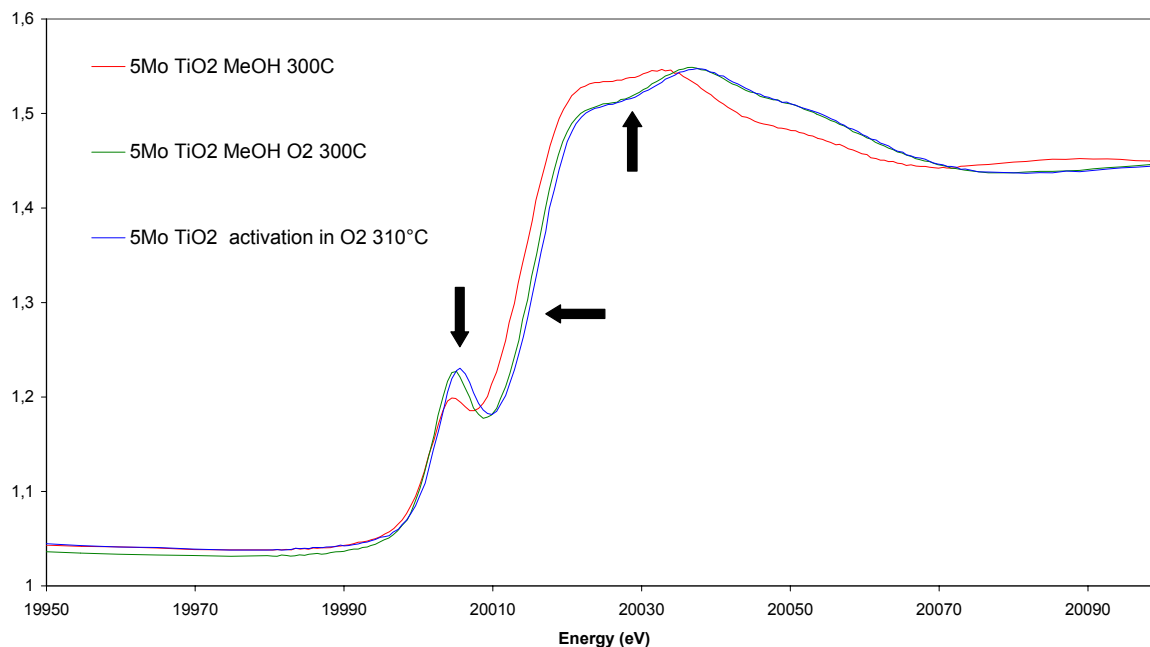

Figure 5: XANES spectra at Mo K-edge of 5% wt.MoO₃/TiO₂ under MeOH at 300°C, 5%wt. MoO₃/TiO₂ under MeOH/O₂ at 300°C and 5%MoO₃/TiO₂ actived at 300°C.

After activation at 300°C in O₂, active molybdic phase is reduced by methanol which leads to an evolution of the XANES signal: shift to the absorption edge towards the low energy and decrease of the pre-edge intensity situated at 20008eV (Figure 5). These evolutions are characteristic of the reduction of the molybdenum species. Then, at 300°C, under a MeOH/O₂ mixture, an almost restoration of the signal obtained after activation of the catalyst is observed, maybe due to the restoration of the oxidative function.

Conclusion

An evolution of the adsorbed species during the synthesis of MoO₃/TiO₂ catalyst has been observed. The Operando study has showed an evolution of the active phase during the oxidation test. The identification of the active phase and adsorbed species during the different steps of the preparation and the reduction require a more in-depth analysis.

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