

Experiment title: STUDY BY XAS OF THE OXIDATION STATE AND LOCAL ENVIRONMENT OF VANADIUM SUPPORTED ON THE MESOPOROUS SILICA USED AS CATALYSTS FOR METHANE OXIDATION

Experiment number:
30-02-706

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BM30B

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Local contact(s): Vivian NASSIF

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Names and affiliations of applicants (* indicates experimentalists):

J.M.M.Millet*,
Institut de Recherches sur la Catalyse CNRS conventionné avec l'Université Claude Bernard, Lyon I, 2

O.V.Safonova*
European Synchrotron Radiation Facility

Report:

The goal of this work was to characterize by XAS at V *K*-edge the oxidation state and local environment of vanadium in V-supported catalysts for methane oxidation to formaldehyde.

We have studied two series of samples: the former corresponds to fresh catalysts with vanadium loading varying from 0.4 wt% (V02) to 2.1 wt% (V12); the latter is V12 sample dehydrated under pure oxygen at 600°C and then hydrated again during different periods of time at room temperature in ambient air. The experiments under vacuum conditions were not successful because vacuum in the cell was not good enough (only 10^{-4} torr) to reduce V12 sample. The XANES spectra obtained for the fresh catalysts are shown in Fig. 1. The spectra were analyzed by the pre-edge peak attributed to $1s \rightarrow 3d$ transition.

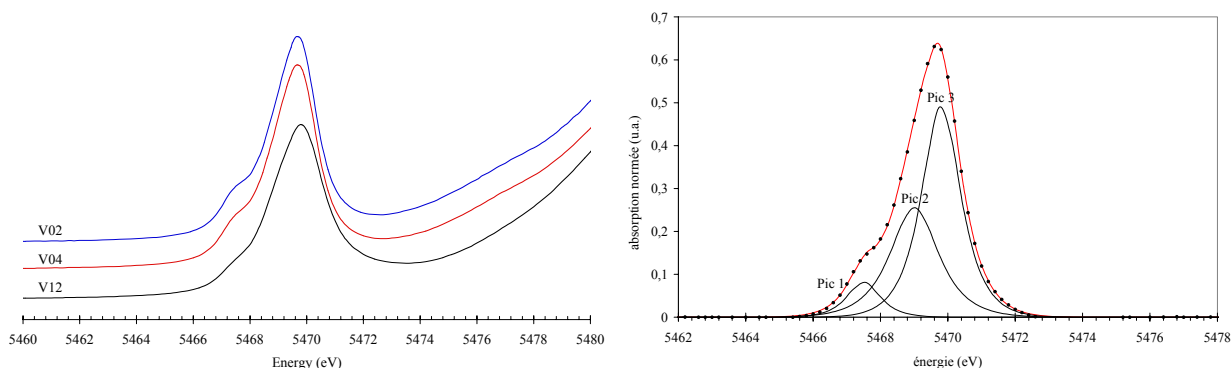


Fig.1 : V pre-edge peaks of V02,V04 and V12 samples (left) and decomposition of the pre-peak of V04 sample (right).

The V pre-edge peak was fitted using three components. The first one (Peak 3 in the Fig. 1) having maximum at 5469.8 eV was attributed to V^{5+} in square base pyramidal coordination (C_{4v} symmetry), whereas the others at 5469.0 and 5467.5 eV were attributed to V^{5+} in distorted tetrahedral coordination (C_{-1} symmetry) (Fig. 2). The distortion of the structure from perfect geometry (T_d) changes the distribution of the LUMO orbitals (mainly having d character) causing the displacement and splitting of $1s \rightarrow 3d$ transitions. The relative amount of V^{5+} in the tetrahedral coordination increase when vanadium content in the sample decrease. Tetrahedral coordination was attributed to vanadium species incorporated in the wall of the mesoporous silica. The presence of such species was indirectly confirmed by TPR experiments showing that some vanadium species were non-reducible by hydrogen even at high temperature. The relative concentration of these species evaluated from TPR data and estimated from the areas of the components in the V pre-edge peak are in a good agreement. The V^{5+} in square base pyramidal coordination has been attributed to polymeric species formed when the solid is hydrated. The existence of these species, which were already observed on silica supported vanadium catalysts, is confirmed by Raman spectroscopy. This method allowed us to observe $V=O$ bond having characteristic vibration at 900-920 nm.

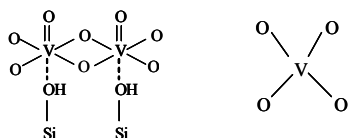


Fig.2 : Schematic representation of vanadium species, which present in the fresh solids.

The XANES spectrum of the V12 compound dehydrated at 600°C in oxygen was collected using *in situ* cell. The goal was to perform further reduction in vacuum in the same cell avoiding the risk of reoxidation. The XANES spectra of hydrated and dehydrated samples are compared in Fig. 3. The intensities of the main peak and its shoulder increase upon dehydration.

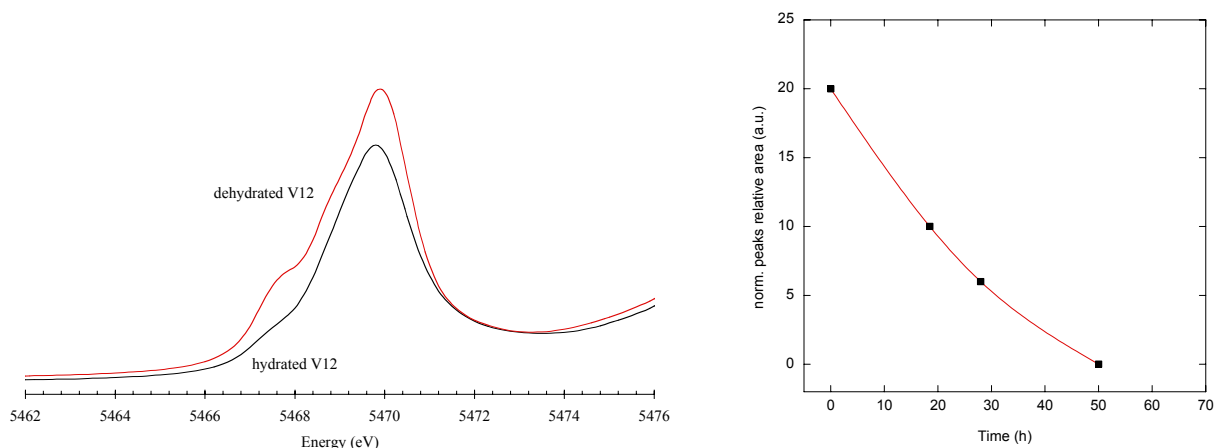


Fig.3 : XANES spectra of the V12 sample before and after dehydration (left). A variation of intensity of the peak vs time of re-hydration process (right).

In the same conditions Raman spectra of the dehydrated sample show that only isolated tetrahedral coordinated species present in the solid. The dispersion of vanadium upon dehydration is confirmed by TPR data; in the final state it is equal to 90%. The pre-edge peak of the dehydrated sample was also fitted using three components. The peak having maximum at 5470.0 eV is attributed to isolated vanadium species with a relatively symmetrical tetrahedral coordination (C_{3v}), whereas the two others at 5468.9 and 5467.6 eV are attributed to the vanadium species already identified in the walls of the silica support and to the species

present at the surface and also having tetrahedral coordination of low symmetry (C_{-1}) (Fig.4). A study by infrared spectroscopy has shown that vanadium species with a V-OH bond at 3658 cm^{-1} were present at the surface of the dehydrated compounds (Fig. 4). They could correspond to the former ones. The re-hydration of the solid at room temperature has been followed in time by recording spectra after 18h30 and 28h. The analysis was done by fitting the spectra with three components. The variation of the area of two components at 5468.9 and 5467.6 eV subtracting the contribution of the species in the wall is shown in the Fig. 3.

The experiments under vacuum conditions were not successful because vacuum in the cell was not good enough (only 10^{-4} torr) to reduce V12 sample

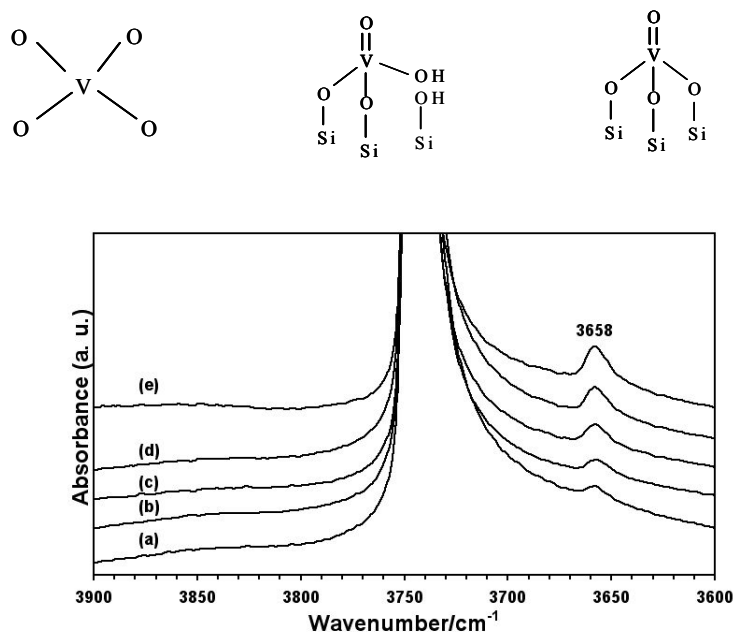


Fig.4 : Schematic representation of the species present in the dehydrated samples and the IR spectra of the samples with increasing vanadium loading (from **a** to **e**) dehydrated under dry O₂ at 550°C.