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Vanadium species in new catalysts for the selective oxidation of methane to formaldehyde: Activation of the catalytic sites

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Abstract

New vanadium oxide supported on mesoporous silica catalysts for the oxidation of methane to formaldehyde were investigated by infrared and Raman spectroscopies to identify and characterize the molecular structure of the most active and selective catalytic sites. *In situ* and operando experiments have been conducted in order to understand the redox and hydroxylation/dehydroxylation processes of the vanadium species. $(SiO)_2VO(OH)$ species were identified in these catalysts in reaction conditions and shown to undergo a deprotonation at 580 °C under vacuum, leading to a site giving a photoluminescence band at 550 nm attributed to reverse radiative decay from the excited triplet state: $(V^{4+}–O^{-})^{*} \leftrightarrows (V^{5+}=O^{2-})$. An activation mechanism of vanadium monomeric species with electrophilic oxygen species is proposed.

Keywords: Supported vanadium oxide; Mesoporous silica; Heterogeneous catalysis; Methane oxidation; Formaldehyde; Operando Raman spectroscopy; *In situ* IR spectroscopy; Hydroxylated monomeric vanadium species; Electrophilic oxygen species

1. Introduction

In the past decade, considerable interest has been shown in developing a process to selectively oxidize methane to formaldehyde or methanol. The challenge facing by the scientists is particularly difficult because of the low reactivity of the starting alkane molecule. However, progress has been made with catalysts corresponding to vanadium oxide supported on silica which are currently the best performing catalysts for the oxidation of methane to formaldehyde [1–5].

Recently, we reported better performances of new catalysts based on vanadium oxide supported on mesoporous silica for partial oxidation of methane to formaldehyde [6]. These catalysts were prepared using a new method based on the co-condensation of vanadium and silica precursor species at neutral pH in a solution containing a template [7]. We confirmed the importance of isolation of the vanadium sites since a higher quantity of vanadium monomeric species was obtained with this method as deduced from TPR curves [6,8]. The presence of two types of monomeric species on the dehydrated surface of our catalysts was also highlighted from Raman and IR experiments [6,8]: these species would correspond to two types of V^{5+} cations (i) with one V=O bond and three bridging V–O–Si bonds and (ii) with one V=O bond, two bridging V–O–Si bonds and one V–OH group. Hydroxylated monomeric species were characterized by an IR band at 3656 cm^{-1} attributed to the ν(VO–H) stretching vibrations, the intensity of which increased with the vanadium content [6,8]. Additionally, it was shown that our preparation method favoured the formation of a higher amount of D2 defects and hydroxylated monomeric species by comparison with a reference V/MCM41 catalyst. It was proposed that the hydrolyzed D2 silica defects could be the preferential anchoring sites for these species [8]. Hydroxylated monomeric species stabilized at the surface of the catalysts around 600 °C would be the most efficient methane oxidation sites explaining the better catalytic activities of the described catalysts.

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In this study, in order to explain the better catalytic properties, we have conducted spectroscopic characterization by IR and Raman spectroscopies focused on the vanadium molecular structure and the other surface species as well as when the catalysts were submitted to various redox treatments at the catalytic reaction temperature under vacuum or directly under reaction conditions with a simultaneous collection of catalytic data by mass spectrometry (operando methodology). In addition to the operando Raman experiments, the characterization of vanadium species after soft reducing treatments was achieved to investigate the redox cycle.

2. Experimental

Vanadium oxide supported on mesoporous silica catalysts have been prepared as described previously [6–8]. A solution containing NH_4VO_3 and cetyltrimethylammonium bromide (C_{16}TMABr) with NH_4Cl (used as a buffer) was first prepared. The pH value of the solution was 5–6 before tetraethoxysilicate (TEOS) was added. The molar proportions of precursors were similar for all the samples (TEOS/NH_4Cl/C_{16}TMABr/H_2O = 0.5/9.2/0.12/130) and only the NH_4VO_3 proportion was varied. After a reflux of the solution for 24 h at 40 °C, the precipitate was filtered and washed with hot water. The template was extracted by washing with ethanol at 80 °C for 2 h. After drying at 100 °C for 12 h, the compound was calcined at 650 °C for 6 h in air flowing at 50 ml min^{-1}. Two samples have been prepared with this method using NH_4VO_3 molar proportions of 0.012 and 20 and characterized in this study. They contained respectively 2.1 and 3.5 wt.% of V and were named 2.1%V/mesoSiO_2 and 3.5%V/mesoSiO_2.

The Raman study was achieved using the violet exciting line at 458 nm of a 2018 RM Ar^+–Kr^+ laser (Spectra physics). The spectra of samples were recorded with a UV–vis–NIR LabRam HR Raman spectrometer (Horiba–Jobin Yvon) equipped with a confocal microscope, Notch filter and CCD detector. The diffused light was spatially dispersed with a 1800 grooves/mm or a 300 grooves/mm diffraction grating. A long working distance objective (×50) allowed focusing of laser and collection of retro-diffused light in the cells. The laser power on the samples was typically 2 mW, conditions under which no significant laser heating was observed.

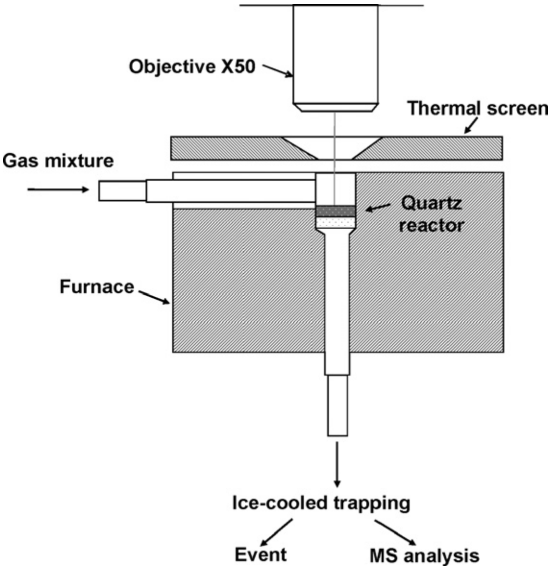

Fig. 1. Schematic representation of the *operando Raman* cell.

Raman spectra were collected during methane oxidation to formaldehyde in the 150–4000 cm^{-1} spectral region. The Raman setup allowing recording spectra of working catalysts is described in Fig. 1. It consists of a homemade furnace containing heating plugs and a specially designed quartz reactor containing a quartz window for light transmission, thermocouple hollow, and inlet–outlet gas connections. The 2.1%V/mesoSiO_2 and 3.5%V/mesoSiO_2 samples were studied by operando Raman. The quality of spectra was poorer for 2.1%V/mesoSiO_2 because of its lower V content and hence only spectra of 3.5%V/mesoSiO_2 are presented in this article. For the operando study, 110 mg of the catalyst were placed in the quartz reactor, which reactor was then introduced into the complementary space of the furnace allowing its support and good thermal exchanges. A thermal screen was finally added to protect the objective. The reaction temperature was varied from 540 to 600 °C under a 90 ml min^{-1} reaction gas flow at atmospheric pressure. The feedstock composition was 40%N_2/13%O_2/38%CH_4/9%H_2O. Steam was obtained using a saturator and the condensable products were trapped in water cooled with ice, and formaldehyde was chemically analysed as described previously [6]. CH_4, O_2, N_2, CO and CO_2 were analysed on-line by a VG ProLab mass spectrometer (Thermo Electron Corporation). No other gas was detected by mass spectrometry. Conversion of methane was determined by following variation of mass 15. A treatment cell with two valves and a quartz window was also used to achieve Raman spectra of powders after treatments at 580 °C under vacuum of 2×10^{-5} mbar or under pure oxygen flow.

Self-supporting disks (about 10 mg cm^{-2}) were prepared by pressing the synthesized samples at 4 bar. They were treated at 580 °C in a homemade infrared cell either under pure O_2 flow at atmospheric pressure, under a vacuum of 2×10^{-5} mbar or under a 40%N_2/13%O_2/38%CH_4/9%H_2O gas mixture at 550 °C at atmospheric pressure. After treatments, the IR spectra were recorded at room temperature with a Fourier transform Vector 22 (Brüker) spectrometer.

EPR has been used for monitoring the generation of O^- radical anions on 2.1%V/mesoSiO2.The results were compared with a conventional 1.7%V/SiO_2 catalyst studied in detail previously [9]. The concentration of oxygen radical anions (O^-, $O_2{}^-$) formed after re-oxidation of reduced catalysts was measured. An ERS-221 spectrometer was used for registration of X-band ESR spectra at variable temperatures. A homemade computer programme (EPR-CAD) was used for processing the experimental data. The samples were placed into quartz ampoules and subjected to standard pretreatment that included several cycles of heat treatment (500 °C) in oxygen (10 Torr) and under vacuum (10^{-6} Torr). This treatment is similar to the sample pretreatment traditionally used by us in experiments performed *in situ* [10,11]. It provides comprehensive cleaning of the surface from adsorbed organic impurities, water and carbon dioxide. After this standard treatment the sample was reduced in 2 Torr H_2 at 500 °C with simultaneous freezing of the products in a trap cooled with liquid nitrogen. Then the sample was evacuated at 500 °C for 30 min followed by cooling to room temperature. After cooling the sample was reoxidized by adsorbing 0.2 Torr O_2 at 25 °C. After the following quick evacuation, the ampoule was sealed. The spectra of oxygen radical anions were measured at room temperature.

3. Results

3.1. Study of the dehydroxylation/rehydroxylation of vanadium species by IR and Raman spectroscopy

Infrared spectra have been recorded on the 2.1%V/mesoSiO$_2$ sample at room temperature after three successive redox treatments. The starting spectrum (Fig. 2a) recorded after a drying and oxidizing treatment under O_2 at 580 °C for 6 h presented an intense asymmetric band at 3740 cm^{-1} attributed to ν(SiO–H) stretching vibrations of silanol groups and a band at 3658 cm^{-1} attributed to ν(VO–H) stretching vibrations of vanadium monomeric species [6,8]. Additionally, it displayed bands around 1630, 1850 and 1960 cm^{-1} (not shown) that correspond to combinations modes and overtones of the silica matrix [12]. After a treatment at 580 °C under vacuum for 4 h (Fig. 2b), the intensity of the band at 3658 cm^{-1} strongly decreased and completely disappeared after 16 h under vacuum (Fig. 2c). The only hydroxylated species were then the silanol groups.

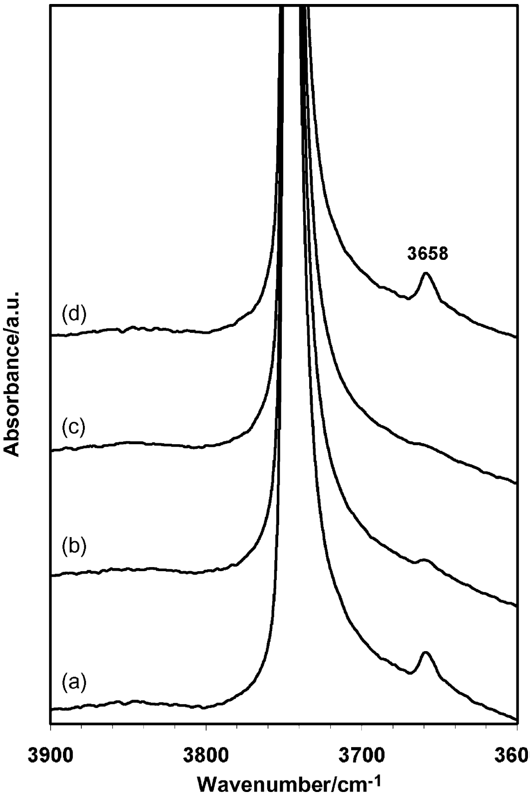

Fig. 2. Infrared spectra of the 2.1%V/mesoSiO$_2$ sample recorded at room temperature after consecutive treatments at 580 °C under: (a) pure O_2 flow for 6 h, (b) vacuum of 2×10^{-5} mbar for 4 h, (c) vacuum of 2×10^{-5} mbar for 16 h and finally (d) pure O_2 flow for 6 h.

The ν(VO–H) stretching band of vanadium monomeric species recovered its initial intensity after a final treatment under O_2 at 580 °C for 6 h (Fig. 2d). Interestingly, this regeneration phenomenon was observed indifferently flowing O_2 or treating statically the sample by filling the cell with O_2 and isolating it. These results clearly demonstrated that a reversible dehydroxylation/rehydroxylation of the vanadium species was taking place during such treatments.

The intensity of the band at 3740 cm^{-1} slightly decreased after each heat treatment indicating consumption of a small amount of silanol groups. In parallel, a small broad shoulder appeared in the second order wavenumber range near 1400 cm^{-1} suggesting a few structural changes of the silica framework.

The same catalyst has been also characterized by Raman spectroscopy after the same consecutive treatments. Two typical spectra recorded with an exciting line at 458 nm are presented in Fig. 3. The spectrum recorded at room temperature after the starting treatment (Fig. 3a) was similar to those obtained at high temperature under O_2. Raman bands were observed at 495, 605, 800, 905, 970, 1038, 1065 and 3738 cm^{-1}. The assignment of all these bands has been previously indicated [6,8]. In particular, the two narrow bands observed at 1038 and 3738 cm^{-1} were respectively attributed to the ν(V=O) stretching vibrations of vanadium monomeric species and ν(SiO–H) stretching vibrations of isolated silanol groups [6,8]. The only difference between the spectra recorded at room temperature and those at high temperature was small shifts of bands. This classical effect for diatomic oscillators arises from the decrease in force constants with increasing temperature due to the anharmonicity of the potential [13].

When the sample was treated under vacuum the spectrum was totally different since only a large and intense photoluminescence band located around 550 nm was observed at room temperature (see the second scale of abscissas for Fig. 3b). This band corresponded to those observed in V-loaded zeolites or mesoporous MCM41 by photoluminescence spectroscopy with an excitation light at 250 nm [14–19]. It was attributed to the

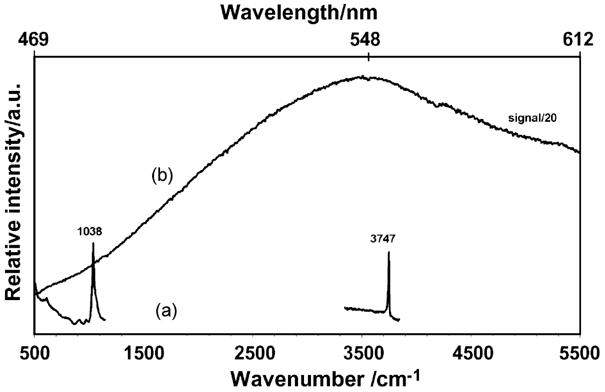

Fig. 3. Raman spectra of the 2.1%V/mesoSiO$_2$ sample recorded at room temperature after consecutive treatments at 580 °C under: (a) O_2 for 6 h, (b) vacuum of 2×10^{-5} mbar for 10 h.

charge transfer $T_1(V^{4+}–O^-)^* \leftrightarrows S_0(V^{5+}=O^{2-})$ of tetrahedral V species [14–19]. The spectrum achieved at room temperature was not superposed by a vibrational fine structure contrarily to those recorded at liquid nitrogen temperature. Interestingly, no photoluminescence band was observed when the samples were directly evacuated under vacuum of 2×10^{-5} mbar without a preliminary dehydrating treatment at high temperature. In that case, the intensity of all the Raman bands decreased especially that at 1035 cm^{-1} in concordance with TPR *in situ* Raman results reported in the literature on V/SiO_2 catalysts [20].

When the sample was further treated under oxygen, it exhibited the same spectrum as after the first heat treatment (not shown for clarity) evidencing that the transformation observed under vacuum was completely reversible.

3.2. EPR study after redox treatments

Fig. 4 presents typical EPR spectra of oxygen radical anions (O^-, O_2^-) formed after O_2 adsorption on 2.1%V/mesoSiO_2 and on the 1.7%V/SiO_2 reference sample reduced at 500 °C. The maximum total concentration of oxygen radical anions on 2.1%V/mesoSiO_2 was about 1.5×10^{18} g^{-1} (Fig. 4a). This value significantly exceeded the maximum concentration (0.6×10^{18} g^{-1}) obtained on the reference compound (Fig. 4b). The same trend was observed after photoreduction of the compounds. The fraction of O^- radical anions in the total concentration of oxygen radicals observed on 2.1%V/mesoSiO_2 was about 30–50%. Such radicals may act as key intermediates in catalytic oxidation processes. As the oxygen radical anions detected were stabilized on monomeric vanadium complexes, the concentration of such complexes on 2.1%V/mesoSiO_2 was much higher than on the reference sample.

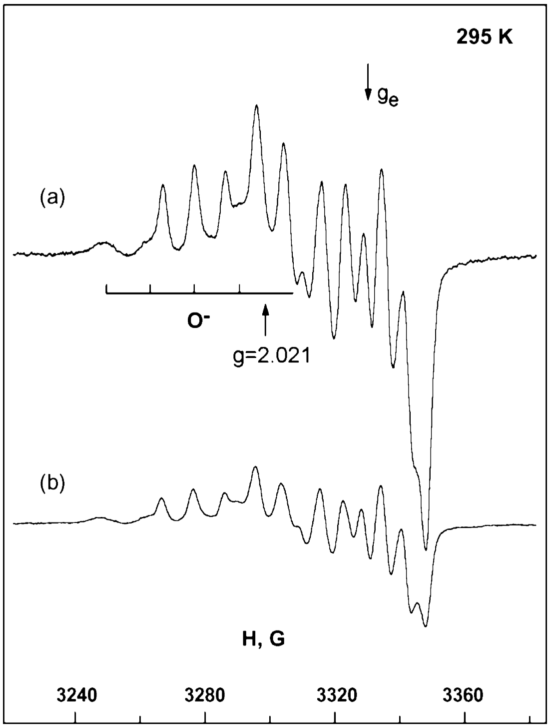

Fig. 4. EPR spectra of: (a) 2.1%V/mesoSiO_2 and (b) the 1.7%V/SiO_2 reference sample after reduction in 2 Torr of hydrogen at 500 °C and re-oxidation at room temperature in 0.2 Torr of oxygen.

3.3. Operando study of the new catalysts by Raman spectroscopy

The new catalysts have been studied by Raman spectroscopy between 540 and 600 °C in the working conditions. Fig. 5 presents the Raman spectra of 3.5%V/mesoSiO_2 recorded at 540 °C (a) and 595 °C (b) under a $O_2/N_2/CH_4/H_2O$ = 13/40/38/9 reaction gas mixture with a GHSV of 54,500 l kg^{-1} h^{-1}. No methane conversion was obtained at 540 °C, whereas it was 7% at 595 °C in the Raman cell. The only detected products after the cell were CO, formaldehyde and traces of CO_2. The selectivity in formaldehyde deduced from chemical analysis was about 35%. These catalytic performances were slightly lower than those obtained by GC chromatography analysis using an optimized reactor (conversion of 7%, CH_2O selectivity of 50% at 590 °C with a GHSV of 132,000 l kg^{-1} h^{-1}). All the spectra recorded between 550 and 600 °C showed the same bands, in particular the bands at 1035 and 3740 cm^{-1} typical of monomeric V^{5+} species and of isolated silanol groups, respectively. However, when the temperature was raised to 595 °C, the band at 3740 cm^{-1} revealed a large, but not intense, shoulder around 3660 cm^{-1} using a low diffraction grating. This shoulder, well-resolved using a high diffraction grating and then located at 3654 cm^{-1} (inserted area in Fig. 5), seemed to correspond to ν(VO–H) stretching vibrations as evidenced by IR spectroscopy. Since monomeric species were mainly present in these catalysts [6,8], this indicated an increase in the number of hydroxylated monomeric vanadium species.

Finally, smaller bands around 2915, 2330 and 1540 cm^{-1} were observed and could be attributed to $\nu_1(CH_4)$ [21], $\nu(N_2)$ and $\nu(O_2)$ stretching vibrations of the gas phase. No methoxy species were observed in working conditions whereas these species characterized by typical intense bands at 665 and 1067 cm^{-1} [22,23] were easily observed when our catalysts were treated under a O_2/CH_3OH gas mixture from 100 to 300 °C.

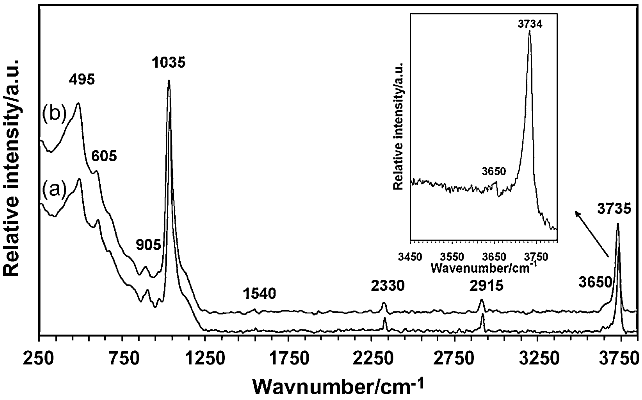

Fig. 5. Operando Raman spectra of the 3.5%V/mesoSiO_2 sample under a $O_2/N_2/CH_4/H_2O$ = 13/40/38/9 reaction gas flow (90 ml min^{-1}) at 540 °C (a) and 595 °C (b) achieved with a diffraction grating of 300 grooves mm^{-1}. The inserted area corresponds to the spectrum obtained at 595 °C with a diffraction grating of 1800 grooves mm^{-1}.

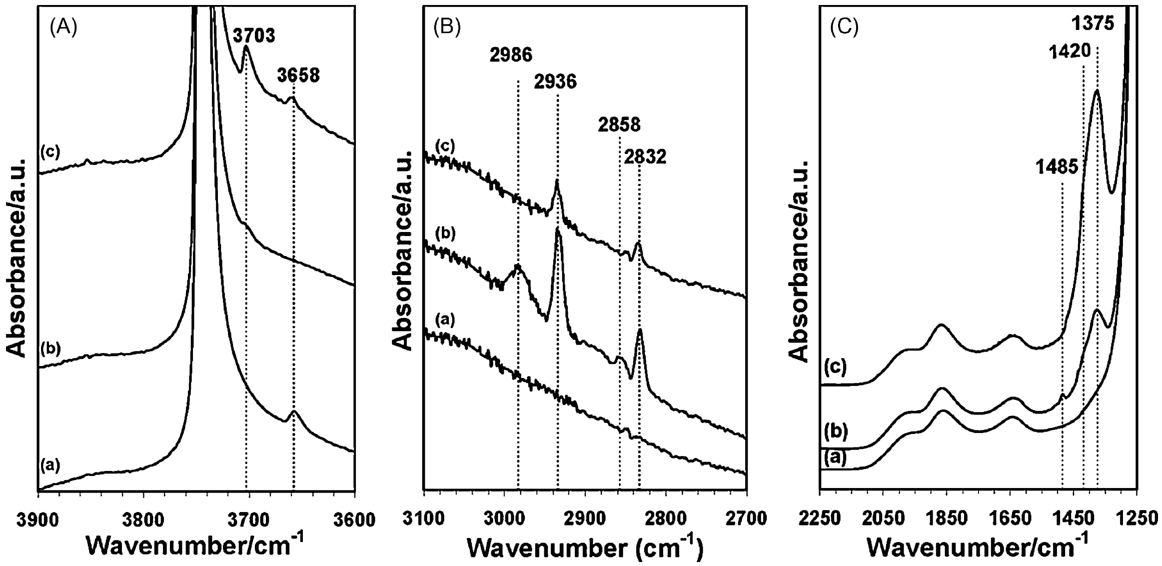

Fig. 6. Infrared spectra of 2.1%V/mesoSiO_2 in the 3900–3600, 3100–2700 and 2250–1250 cm^{-1} ranges after treatments at 550 °C under: (a) O_2 for one night, (b) a $N_2/CH_4/O_2$: 60/30/10 reaction gas mixture for 5 h and (c) a $N_2/CH_4/O_2/H_2O$: 58/29/9/4 reaction gas mixture for 5 h.

3.4. Characterization by infrared spectroscopy after treatments under reaction mixture

Since it was not possible to study the catalysts directly by infrared spectroscopy in the reaction conditions, we have recorded spectra of the 2.1%V/mesoSiO_2 sample after treatments under reaction mixture. The sample was maintained at 550 °C for 5 h under a flow with the composition $N_2/CH_4/O_2 = 60/30/10$ or $N_2/CH_4/O_2/H_2O = 58/29/9/4$ to study the effect of water partial pressure. The spectra obtained are reported in Fig. 6b and c, respectively and compared to the spectrum of the sample dehydrated under O_2 for one night at the same temperature (Fig. 6a). After the treatment under the reaction conditions without water, new bands at 2983, 2936, 2858 and 2832 cm^{-1} appeared (part B). These bands were attributed to $VOCH_3$ and $SiOCH_3$ species formed at the surface of the catalysts [22,24,25]. The strong decrease in intensity of the bands at 3740 and 3658 cm^{-1} (part A) suggests the participation of both VOH and SiOH groups in methoxy formation. Co-feeding of water induced a strong decrease in the relative intensity of the bands due to methoxy species (Fig. 6c). The band at 3658 cm^{-1} was again observed and a new band was detected at 3703 cm^{-1}. This band, which was also observed when the sample was treated under a mixture of O_2 and H_2O has been clearly attributed to new Si–OH species with an acidic character formed at high temperature [8]. Two additional second order bands were then observed at 1375 and 1420 cm^{-1}. These bands could arise from slight structural changes of the silica framework under steam. This evolution seemed to be irreversible since after further heat treatment of the 2.1%V/mesoSiO_2 sample at 550 °C overnight under pure O_2, the bands remained unchanged. The slight evolution of catalytic performances observed for the first testing hours may be related to the appearance of these bands [6].

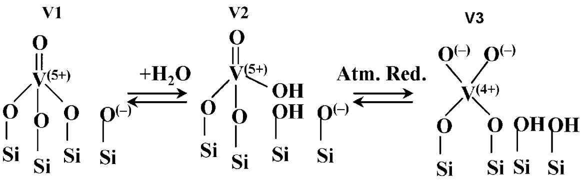

Fig. 7. Schematic equilibriums between non-hydroxylated (V1) and hydroxylated (V2) species and between hydroxylated (V2) species and proposed active sites (V3).

4. Discussion

Raman spectra achieved under working conditions indicated an increase in the number of hydroxylated monomeric vanadium species. It has been proposed in a previous article that these species were $(SiO)_2VO(OH)$ with two bridging bonds [8]. The observation of these species in working conditions implies that vanadium cations are pentavalent at stationary state. The observed stability of the fully oxidized state during the partial oxidation of methane to formaldehyde could arise from a fast reoxidation of vanadium active site during its redox cycle [26].

Nevertheless, it should be recalled that the observation of $(SiO)_2VO(OH)$ species in working conditions does not demonstrate their implication in the catalytic reaction and it is still possible that they are only spectators. However, it was shown that a higher proportion of $(SiO)_2VO(OH)$ species was obtained with our preparation method leading to better catalytic activities for oxidation of methane to formaldehyde [8]. The positive effect of water co-feeding on catalytic performances was also explained by the increase in the number of $(SiO)_2VO(OH)$ vanadium species [8]. Indeed, the equilibrium between non-hydroxylated and hydroxylated species (Labelled V1 and V2, respectively) could be displaced to the right under steam at the reaction temperature (Fig. 7).

The *in situ* characterization of the new catalysts showed that both hydroxylation/dehydroxylation and oxidation/reduction processes of catalytic sites were strongly associated. We observed that under vacuum the $(SiO)_2VO(OH)$ species were dehydroxylated. Two mechanisms may explain such dehydroxylation, (i) a reaction with a neighbouring silanol group and the formation of a three Si–O–V bonded species or (ii) a proton migration from the VOH group to the support. From mechanistic point of view, the fact that the SiOH surface concentration decreases in parallel to the V species dehydroxylation would be in favour of the first mechanism. However, such a decrease was also evidenced by IR spectroscopy when the catalyst was subsequently treated under O_2 + 15% H_2O at 590 °C. Considering the first mechanism, only V^{5+} vanadium species should be present after vacuum treatment, what was not observed since (V^{4+}–O^-) groups were evidenced by Raman spectroscopy. Therefore, the second mechanism was favoured.

The results obtained showing the regeneration of the $(SiO)_2VO(OH)$ species after a consecutive treatment under dry oxygen support the second mechanism based upon a proton migration without water involvement. A change in the surface potential energy and in silanols content or their distribution on the silica would be the driving force for the migration of the proton from the VOH group to the support.

The vicinity of strained D2 defects may also help the activation of hydroxylated monomeric vanadium species. Actually, the results presented in our previous paper showed that the hydroxylated monomeric species were preferentially anchored at D2 defects, which concentration was enhanced by the new preparation method [8]. The strained three-fold rings called D2 could be a preferential site in silica for creation of dangling bond defects with an unpaired electron. For instance, it was shown that the efficiency of creation of dangling silicon bonds and dangling oxygen bonds strongly correlates with the number of D2 defects by photolysis [27] according to:

$$\equiv\mathrm{Si{-}O{-}Si}\equiv \rightarrow \equiv\mathrm{Si{-}O}^{\bullet} + {}^{\bullet}\mathrm{Si}\equiv \qquad (1)$$

From all the results, we suggest a reaction mechanism involving both hydroxylated monomeric vanadium site and surface silica defects for the methane oxidation to formaldehyde (Fig. 7): Upon dehydroxylation of the support, a change in surface potential energy would lead to the V3 species with an electron delocalization as proposed in Fig. 7. The two electrophilic oxygen species present could activate homolytically the C–H bond of methane and lead to the formation of VOH and $VOCH_3$ species. This type of mechanism involving O^- species is frequently assumed for oxidation over V and Mo oxide catalysts as reviewed in [28]. Infrared spectroscopy allowed identification of methoxy species when the catalysts were quenched from the reaction temperature. Similarly, methyl radicals formed by the thermal decomposition of azomethane reacted with V_2O_5 at 30 °C to form methoxy groups [29]. However, our attempts to detect these species *operando* have unfortunately failed. Presumably, their lifetime at the surface of the solids might be too short and their number could also be limited. Studies made in TAP reactor tend to confirm a very weak interaction between the catalyst and CH_4 that is activated through interaction with an electrophilic oxygen species [30].

5. Conclusion

In this study, *in situ* and operando experiments have been achieved in order to identify active and selective vanadium species in new catalysts efficient for methane oxidation to formaldehyde. Hydroxylated monomeric $(SiO)_2VO(OH)$ species were observed in these catalysts in reaction conditions.

The presence of D2 defects is proposed not only to favour anchoring of $(SiO)_2VO(OH)$ species during thermal activation but also to be involved in the hydroxylation/dehydroxylation process of the isolated vanadium species. The presence of these defects in higher proportion in the new catalysts than on similar catalysts prepared differently, may explain the higher catalytic performances of the new catalysts.

Finally, an activation mechanism has been suggested from *in situ* characterization after soft redox treatments. It would imply electrophilic defects of silica at the vicinity of the hydroxylated monomeric vanadium species that would favour activation of vanadium species with electrophilic oxygen species.

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