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Vanadium species in new catalysts for the selective oxidation of methane to formaldehyde: Specificity and molecular structure dynamics with water

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Abstract

Mesoporous VO_x/SiO_2 catalysts prepared with a novel method appear to be more efficient for partial oxidation of methane to formaldehyde. In this study, vanadium species present in these catalysts were characterized by TPR measurements, in situ IR and Raman spectroscopies after various high-temperature treatments. The molecular structure of vanadium species appeared to be dynamic with a reversible strong evolution between the hydrated state in ambient air and the dehydrated and dispersed one. Raman and IR spectroscopies allowed identification of the presence of hydroxylated monomeric species under dehydrated conditions. The novel preparation method favored the formation of a greater number of D2 defects compared with a reference V/MCM41 catalyst. In addition, quantitative IR measurements have shown that a higher proportion of these monomeric hydroxylated species was obtained with this method, leading to the conclusion that the hydrolyzed D2 silica defects could be their preferential anchoring sites and that these species would be the most efficient methane oxidation sites, explaining the better catalytic activities of the described catalysts. The positive effect of a water co-feed on catalytic performance was explained by an increase in the number of hydroxylated monomeric species present under steam at the reaction temperature. A structure for the monomeric hydroxylated species is proposed and discussed.

Keywords: In situ Raman spectroscopy; In situ IR spectroscopy; Molecular structure; Hydroxylated monomeric vanadium species; Silica defects; Partial oxidation; Methane; Formaldehyde

1. Introduction

The valorization of natural gas through new oxidation processes has been the focus of intensive study over the past two decades. Among the proposed processes, the direct partial oxidation of methane into formaldehyde shows strong potential [1–8]. This process can contribute to the global effort to find other sources of hydrocarbons and preserve crude oil stocks, providing a cleaner process that leads to better environmental preservation. However, to provide industrial feasibility and be economically viable, the process needs to be very selective at nonnegligible conversion. Such requirements have not yet been reached, but constant progress is being made.

The most active and selective catalysts for the direct oxidation of methane to formaldehyde are based on Mo or V oxides supported on silica. Methods to improve the activity or selectivity of these systems has been proposed based on factors affecting the active-phase composition, the support structure, or the catalyst activation procedure. Most studies performed thus far agree on two key factors that appear essential to high performance: dispersion of the active sites to favor isolated species and the method of preparing the silica support (although the latter is less well understood). In this latter case, the density of strained siloxane bridges or of impurities such as Fe^{3+} coming from the starting siliceous precursor has been proposed to explain the effect of the preparation method [9,10].

We have recently reported a new method to obtain more efficient catalysts corresponding to vanadium oxide supported on mesoporous silica [7]. We confirmed the importance of isolation of the vanadium sites, because a greater quantity of vanadium monomeric species was obtained with this method. The

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presence of hydroxylated monomeric species in these catalysts was also revealed by Raman and IR experiments.

In the present study, we investigated the molecular structure of these highly dispersed VO_x/SiO_2 catalysts under various states (hydrated, dehydrated, steam-treated) by in situ Raman and IR spectroscopies and temperature-programmed reduction (TPR). This study had two goals: investigating the interaction of isolated vanadium species with the silica surface defects and gaining insight into (through a comparative study with a catalyst of the same type prepared using a classical procedure) why these new catalysts are more efficient for methane oxidation to formaldehyde. The results obtained lead us to discuss the nature of the most active monomeric species present at the surface of the catalysts.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared according to a patented procedure [11]. Three solutions were first prepared by dissolving NH_4VO_3 (Sigma, >99.7%) in 5 ml of water, 2.72 g of cetyltrimethylammonium bromide (C_{16}TMABr, Alfa Aesar, >99%) in 50 ml of water, and 30.27 g of NH_4Cl (Prolabo, >99.5%) used as a buffer in 90 ml of water. These solutions were mixed, and the pH value of the resulting solution was adjusted to 5–6 before tetraethoxysilicate (TEOS, Fluka, >99%) was added. The TEOS/NH_4Cl/C_{16}TMABr/H_2O/NH_4VO_3 molar proportions were equal to 0.5/9.2/0.12/130/y, with y varying from 0.002 to 0.040. After the solution was refluxed for 24 h at 40 °C, the precipitate was filtered and washed several times 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 under flowing air (50 ml min^{-1}). The various catalysts prepared were referred to their y value; for example, V16 was prepared with $y = 0.016$. Compound without vanadium was also prepared through this route and was labeled “support.” X-ray diffraction analysis of the synthesized samples and measurements of their surface areas (BET method) and pore sizes (BJH method) have been reported previously [7].

One reference sample, labeled V/MCM41, was prepared following an impregnation method as described previously [12]. The MCM41 support was first synthesized according to a published method [13] and then pretreated under vacuum before impregnation with a NH_4VO_3 solution. The compound was dried at 120 °C for 8 h and calcined at 600 °C in air for 16 h. It contained 2.8 wt% of V.

2.2. Catalyst characterization

XPS spectra were recorded on a Axis Ultra (Kratos Analytical) spectrometer using AlK_α exciting radiation at 1486.6 eV, a pass energy of 160 eV, and a 1-eV stepped increase from 0 to 1200 eV. TPR curves were recorded from room temperature up to 900 °C by heating at 3 °C min^{-1} under a 1% H_2–Ar gas mixture. The amounts of consumed H_2 were determined by gas chromatography with TCD detection. Before analysis, all of the samples were pretreated in oxygen at 570 °C for 6 h. Pretreatment of the V20 sample at 400 °C for 4 h was done for comparison purposes.

Raman spectra of the samples were recorded with a LabRam HR Raman spectrometer (Horiba-Jobin Yvon) equipped with a confocal microscope. The 514.53 nm exciting line of a 2018 RM Ar^+–Kr^+ laser (Spectra Physics) was focused using a ×50 long working distance objective. The spectra collected using an 1800 grooves mm^{-1} grating were accurate within 2 cm^{-1}. The spectral evolution with the laser power was previously examined to determine the most suitable power. Thus, a power on the samples of 2 mW was usually chosen. However, spectra at room temperature in air were recorded at a power of only 150 μW under a microscope, to avoid dehydration. In situ Raman spectra were achieved using a THMS600 cell (Linkam) at various temperatures in air or under gas flux. Steam was added by bubbling pure oxygen in a heated water saturator. All of the experiments were conducted on different points of the samples several times, and the same evolutions were observed.

Self-supporting disks (about 10 mg cm^{-2}) were prepared for in situ infrared examination by pressing the powders at a pressure of 4 bar. The pellets were treated for a long time in a homemade infrared cell at 580 °C in flowing pure oxygen or a O_2/3–4% H_2O mixture obtained using a water saturator at room temperature. The water vapor treatment was systematically followed by a purge of the cell in a flow of pure oxygen at 580 °C. After treatment, spectra were recorded at room temperature with a FTIR Vector 22 (Brücker) spectrometer.

2.3. Oxidation of methane

Oxidation of methane was carried out at atmospheric pressure in a conventional flow apparatus as described previously [7]. The organic reactant and the reaction products were analyzed on-line by gas chromatography with a TCD. Methane, formaldehyde, methanol, and CO_2 were separated on a Hayesep T column and O_2, N_2, and CO were reported on a molecular sieve column. The reaction temperature ranged from 550 to 600 °C. A feed composition of $O_2/N_2/CH_4/H_2O$: 13/40/38/9 was used with a gas hourly space velocity (GHSV) of 109,300 L kg^{-1} h^{-1}.

3. Results and discussion

3.1. Characterization of the fresh and used catalysts

The fresh and used catalysts have been characterized by X-ray diffraction (XRD), specific surface area, and pore size measurements as reported in a recent paper [7]. All of the values of the specific surface areas were around 1000 $m^2\,g^{-1}$, and all of the powder XRD patterns showed only a broad peak at around $2\theta = 1.7°$–$2.0°$ ($d = 4.4$–5.2 nm), assigned to the (100) reflection. These data are typical of poorly ordered mesoporous materials. A slight decrease in the peak’s intensity and an increase in its width were systematically observed after catalytic testing. This loss of crystallinity was accompanied by a decrease in specific surface area (from 1000 to 825 $m^2\ g^{-1}$), which may be related to a slight loss of catalytic activity with time on stream over the first 40 h. In any case, the catalyst performances reported in Table 2 were obtained after stabilization of activity.

3.2. Molecular structure dynamics of the new VO_x/SiO_2 catalysts with temperature and water

To investigate the molecular structure of the new highly dispersed VO_x/SiO_2 catalysts, characterization was undertaken by Raman spectroscopy in ambient air and at high temperature under a dry or moist atmosphere. In the two latter cases, because IR spectra could not be recorded in situ at high temperature, the characterization by IR spectroscopy was achieved at room temperature after treatment at high temperature.

3.2.1. Characterization of the VO_x species in ambient air

The Raman spectrum of the V20 sample hydrated in ambient air is shown in Fig. 1a. All the bands of this spectrum are very similar to those of $V_2O_5{\cdot}nH_2O$ xerogels [14,15]. This spectrum is notably characterized by Raman bands at 700 and 505 cm^{-1} attributed to the V–O–V stretching mode [16]. The presence of these bands has been linked to V cations that may share corners and edges to form chain polymers and/or a 2D VO_5 layer similar to those existing in $V_2O_5{\cdot}nH_2O$ xerogels [14,16]. The same feature was previously reported by Gao et al. with a hydrated V_2O_5/SiO_2 catalyst [16]. It can be postulated that hydration process leads to vanadium oxide species lying on the support without V–O–Si bridging bonds. At the hydrated state, the nature of vanadium species would be mainly determined by the PZC of the siliceous support and only slightly by the structural properties of this support.

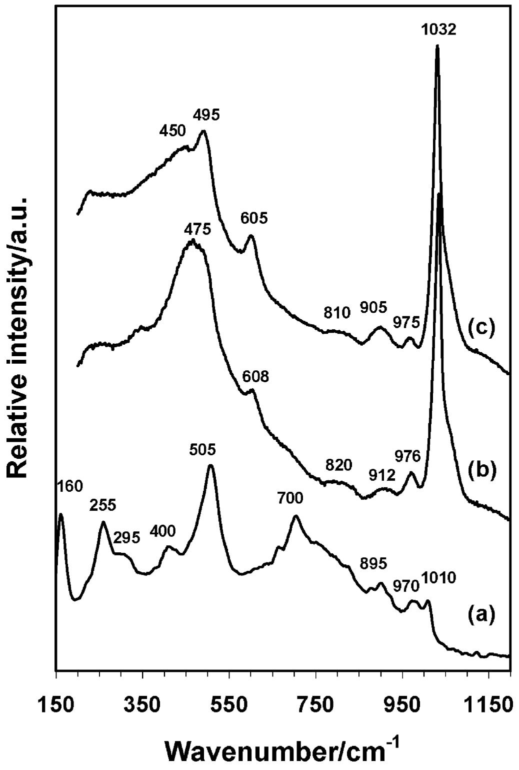

Fig. 1. Raman spectra of the V20 catalyst at various temperatures in air: (a) 20, (b) 400, and (c) 600 °C.

3.2.2. Characterization of the VO_x species at high temperature under a dehydrated atmosphere

The catalyst dehydration process was studied by recording two consecutive spectra in air at 400 and 600 °C (Figs. 1b and 1c). The first observation at the macroscopic level was that the dehydration of the V20 catalyst induced a change of color from yellow to white. This feature, observed for almost all V/SiO_2 catalysts, is due to the change of vanadium coordination from distorted octahedral to tetrahedral, leading to the absence of absorption band in the visible spectral range [12,17–19]. The dehydrated catalyst spectra (Figs. 1b and 1c) differed greatly from the spectrum of the hydrated catalyst (Fig. 1a), indicating that the molecular structure of the vanadium oxide species depends strongly on the degree of hydration. The spectra show an intense band located at 1035 cm^{-1} at 400 °C (Fig. 1b) and slightly downshifted to 1032 cm^{-1} (Fig. 1c) at 600 °C. This band can be attributed to the stretching vibrations of short V=O bonds of isolated distorted vanadium tetrahedra [16,18,20–23]. This observation implies that the catalyst dehydration causes depolymerization of $V_2O_5{\cdot}nH_2O$ xerogels, leading to dispersion and anchoring of the vanadium oxide species [16,24].

We previously proposed from IR results the presence of two types of monomeric species on the dehydrated surface of our catalysts [7]. These species correspond to two types of V^{5+} cations, one type with one V=O bond and three bridging V–O–Si bonds and another type with one V=O bond, two bridging V–O–Si bonds, and one V–OH group. As a result of the existence of two monomeric species, their ν(V=O) bands positions should be close, because only one ν(V=O) band can be clearly distinguished in the Raman spectra of the dehydrated catalysts (Figs. 1b and 1c). The V–OH groups have been well characterized by an IR band at 3656 cm^{-1} attributed to the ν(VO–H) stretching vibrations [12,18,19,23,25,26]. This attribution is also reinforced by the linear intensity increase of this band with increasing vanadium content; no impurity can explain the formation of hydroxyl groups susceptible to appear in the IR spectra with the intensity observed here [7]. Recall that the starting precursors for the preparation of the catalysts were highly pure, especially the vanadium precursor. In addition, XPS spectra did not reveal the presence of impurities at amounts >0.1 at%. As only monomeric species were evidenced by Raman spectroscopy, the IR band at 3656 cm^{-1} has been attributed to hydroxylated monomeric species [7]. The stabilization of these V–OH groups at the surface of the catalysts dehydrated at 600 °C in dry O_2 was demonstrated since no band around 3540 cm^{-1} corresponding to vibrations of water were observed in the spectra [7].

The broad bands observed near 810 and 450 cm^{-1} at 600 °C (Fig. 1c) were assigned to ν_s(Si–O–Si) stretching and δ(Si–O–Si) bending modes [27] and the shoulder present around 1060 cm^{-1} to $\equiv$Si(–O$^-$) [28]. The bands observed near 495 and 605 cm^{-1} at 600 °C were assigned to D1 and D2 defect modes, respectively, due to cyclic siloxane species vibrations (4- and 3-

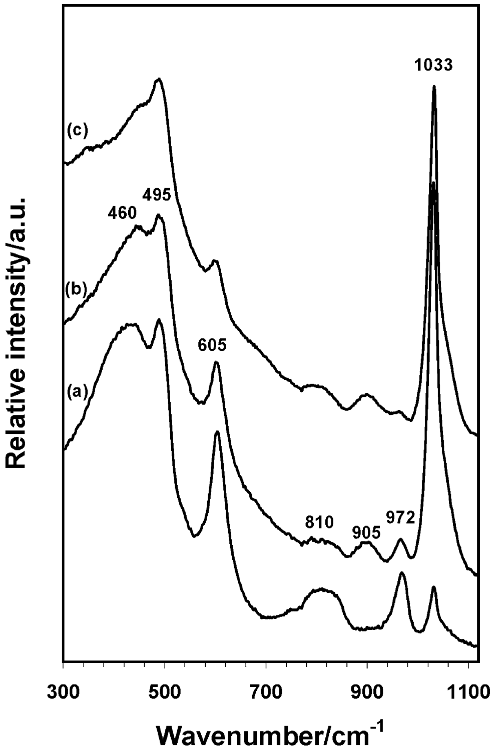

Fig. 2. Raman spectra of: (a) V02, (b) V16, and (c) V/MCM41 catalysts at 600 °C in air.

membered rings) [16,27,29], and the band near 970 cm^{-1} was assigned to ν(Si–OH) elongations of silanol groups [16,18,30].

Modifications in the Raman spectra were observed on heating above 400 °C: at first, the intensity of the band due to silanol groups strongly decreased, whereas the intensities of bands D1 and D2 both increased. This suggests formation of the tri- and tetracyclosiloxane rings via condensation of surface silanol groups, as reported previously [16,31–33]. Another notable phenomenon was the significantly increased intensity of the band near 905 cm^{-1}. The assignment of this band is still under active discussion. Several authors have assigned this band to $((VO_3)_n)^{n-}$ polymeric metavanadate chains [18,20, 34], whereas others have assigned it to $=Si(-O^-)_2$ [28] resulting from silica perturbations due to anchoring of surface vanadium oxide species [16,22]. Recently, the band observed at around 915 cm^{-1} was assigned from DFT calculations to O–O stretching vibrations of chemisorbed $O_{support}-V=O(O_2)$ species [35,36]. The authors explain the high broadness and low intensity, which are unusual for a peroxo stretching mode, by thermal movements of the bound oxygen molecule at room temperature. In the present study, it appears that this band was intense at 600 °C in air, and, consequently, the involved species had to be stable in these conditions, which should not be the case for the peroxo species. More convincingly, the band at 905 cm^{-1} was attributed to ν(V–O–Si) stretching modes based on experimental and theoretical studies [37,38].

Fig. 2 compares the Raman spectra of V02 (a) and V16 (b) catalysts at 600 °C in air. An increase in vanadium content strongly influenced the shape of the Raman spectrum; the intensity of the ν(V=O) band of monomeric species at 1033 cm^{-1} increased, whereas that of the ν(Si–OH) at 972 cm^{-1} decreased, indicating an anchoring of vanadium species by silanol group consumption [7]. In addition, the quantity of the D2 defect band decreased, suggesting preferential anchoring of vanadium species on these sites [16]. These defects can be readily hydrolyzed [27], giving rise to two vicinal silanol groups in which species with two V–O–Si bridging bonds can be easily formed. The framework structure would have an effect on the structural and chemical properties of anchored vanadium species [39]. Finally, a band at 905 cm^{-1} was observed on the Raman spectrum of V16 (Fig. 2b) but was almost absent on the spectrum of V02 (Fig. 2a). Enhancement of the band at 905 cm^{-1} with the vanadium content was consistent with its attribution to ν(V–O–Si) stretching vibrations [37,38], because the number of (V–O–Si) bonds increased. The poorly resolved band at around 690 cm^{-1} could be due to modifications of silica vibrations with increased V loading.

Finally, it should be emphasized that the molecular structure dynamic observed on heating is completely reversible, because the spectrum recorded after rehydration in ambient air was similar to the initial one.

The new VO_x/SiO_2 catalysts with various amounts of vanadium were characterized by TPR after undergoing a dehydrating pretreatment under oxygen at 570 °C for 6 h. The TPR curves contained one narrow, intense peak at around 550 °C attributed to isolated species and a diffuse, weak peak at higher reduction temperatures possibly due to nonisolated species [7]. The amounts of hydrogen consumed by isolated species and the dispersion values are plotted versus the vanadium content in Figs. 3A and 3B, respectively. The amount of hydrogen consumed by isolated species was deduced precisely from the surface area of the low-temperature TPR peak [12,40–43]. The dispersion values were calculated by dividing the area of the low-temperature TPR peak by the area of the total TPR profile as proposed previously [44,45]. The amount of isolated species increased linearly up to a vanadium content of ca. 3 wt%. Only low amounts of hydrogen consumed by nonisolated species were detected; thus, the dispersion values were high (>80%). In addition, Fig. 3A shows that the amount of hydrogen consumed by the isolated species reached zero when the total vanadium content was equal to 0.2 wt%, suggesting the presence of small amounts of nonreducible vanadium species located in the silica walls. For a vanadium content >3 wt%, the amount of isolated species remained constant while the dispersion values dropped to around 50% (Fig. 3B) due to an increasing amount of nonisolated species. Therefore, our synthesis method only allowed isolation of a limited number of vanadium species, corresponding to a V content of 3 wt% and a surface concentration of 0.35 V/nm^2. This maximum amount could be determined by the intrinsic properties of the synthesized silica support, particularly the quantity and location of silanol groups in defect sites [16,46].

The V16 catalyst was also characterized by TPR measurements after pretreatment in oxygen at 400 °C. The amount of hydrogen consumed by isolated species and the dispersion value were compared with those of the catalyst dehydrated at 570 °C (Table 1). The isolation level decreased with increasing

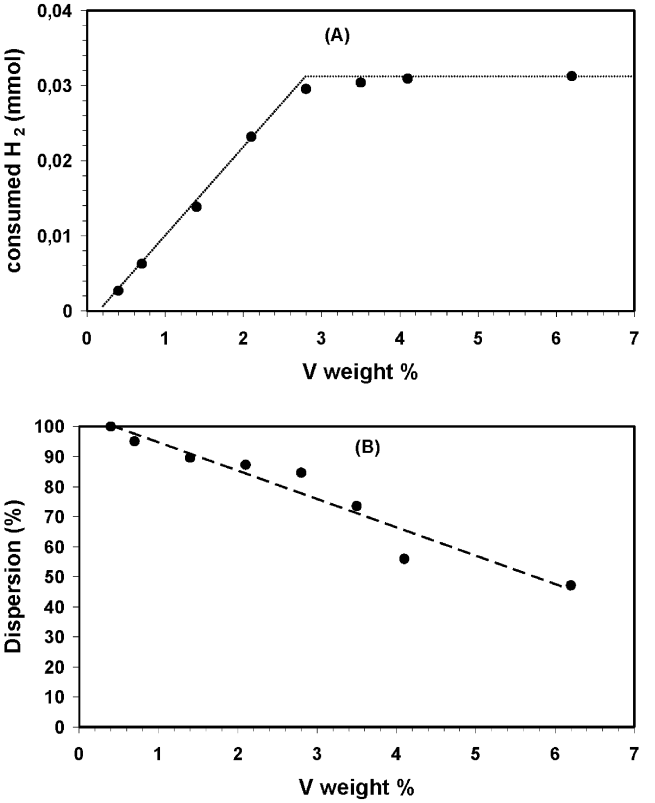

Fig. 3. (A) H_2 consumed by isolated species and (B) dispersion versus V amount (weight %) deduced from TPR curves of the VO_x/SiO_2 catalysts.

Table 1
H_2 consumed by isolated species and vanadium dispersion of the V16 and V/MCM41 catalysts

Sample	Pretreatment in O_2	H_2 consumed by isolated V species (mmol)	V dispersion (%)
V16	4 h at 400 °C	0.051	93
V16	6 h at 570 °C	0.030	85
V/MCM41	6 h at 570 °C	0.024	76

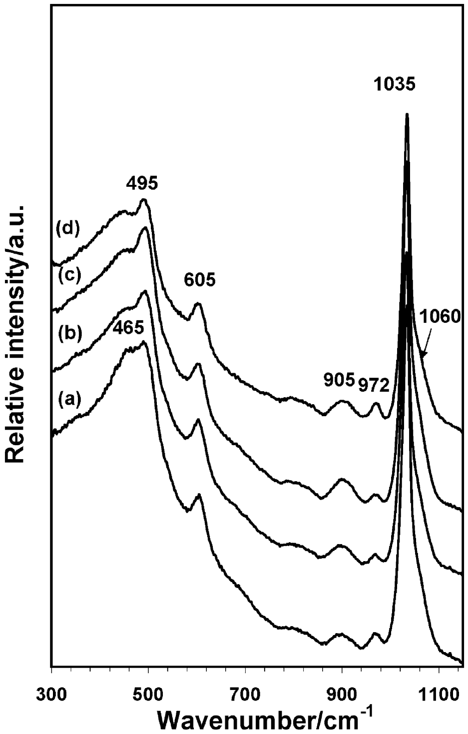

Fig. 4. Raman spectra of the V20 catalyst recorded at 600 °C under flowing: (a) O_2 just after reaching this temperature, (b) O_2 for 4 h, (c) O_2 containing 10% H_2O for 12 h, and (d) directly heated under flowing $O_2 + 10\%$ H_2O for 12 h.

pretreatment temperature. This may be explained by the condensation of two vicinal hydroxylated monomeric species at high temperature, leading to the formation of dimeric species through the removal of water.

3.2.3. Characterization of the VO_x species at high temperature under a hydrated atmosphere

The steam effect on the molecular structure of the dehydrated catalysts at the reaction temperature was studied by combining in situ Raman and infrared spectroscopy, in an effort to understand the improved activity resulting from steam co-feeding during catalytic testing at around 600 °C. It was previously observed that methane conversion increased by 50% with increasing water pressure up to 8 kPa [7]. An optimum formaldehyde yield was then seen at this partial pressure.

Raman spectra recorded at 600 °C showed slight structural evolutions of the V20 catalyst with time under flowing dry oxygen at high temperature (Figs. 4a and 4b). Indeed, a slight increase in the intensity of the bands located around 905 and 495 cm^{-1} and a decrease of the band at 972 cm^{-1} were observed. The evolution of the band at 905 cm^{-1} could be linked to the transformation of some hydroxylated monomeric species into nonhydroxylated monomeric species in dry conditions, whereas that of the other bands (at 495 and 972 cm^{-1}) could correspond to the dehydroxylation of silica by either Si–O–Si or $\equiv$Si(–O$^-$) formation.

The consecutive addition of steam in the treatment atmosphere had no significant affect on the relative intensity of the bands at 905, 690, and 972 cm^{-1} (Fig. 4c). Inversely, when the sample was directly steam-treated from room temperature up to 600 °C, the number of silanol groups remained much higher (Fig. 4d), suggesting that thermal activation of the catalyst under steam can avoid the dehydroxylation of silica. No significant difference in the final intensity of the band at 905 cm^{-1} between the two steam treatments was observed, indicating the presence of a similar number of (V–O–Si) bonds.

Fig. 5 presents the infrared spectrum between 1300 and 2300 cm^{-1} (part A) and between 3600 and 3800 cm^{-1} (part B) of the V12 catalyst recorded at room temperature after the following consecutive treatments (a) dehydration of the sample under oxygen at 580 °C for 12 h; (b) treatment under oxygen containing 3–4 vol% water vapor at 580 °C for 6 h, followed by evacuation under oxygen for 6 h; and (c) evacuation under oxygen for 44 h. For comparison, the siliceous support was treated under oxygen containing 3–4 vol% water vapor at 580 °C for 6 h and then under oxygen for 24 h (d).

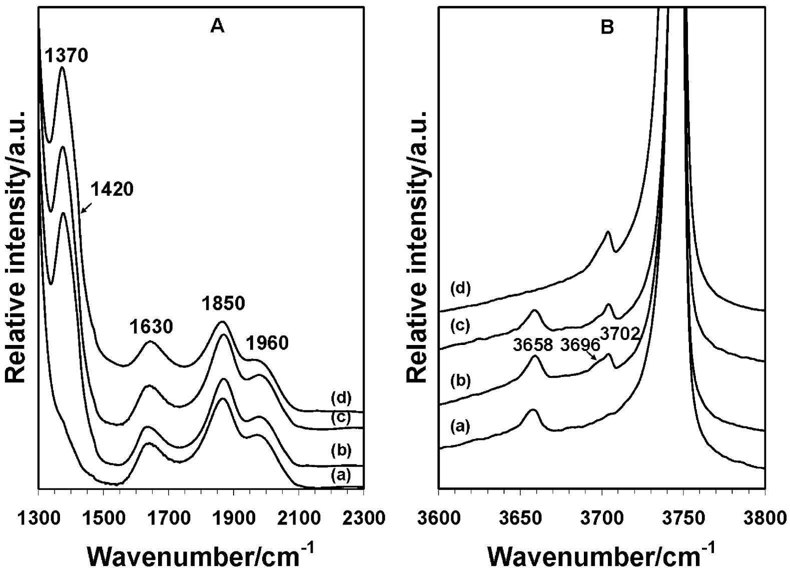

Fig. 5. Room temperature IR spectra of the V12 catalyst after consecutive treatments at 580 °C under flowing: (a) O_2 for 12 h, (b) O_2 containing 3–4% H_2O and then evacuated under O_2 for 6 h, and finally (c) evacuated under O_2 for 44 h. The IR spectrum of the support alone after treatment at 580 °C under O_2 containing 3–4% H_2O and then evacuated under O_2 is reported for comparison (d).

All of the IR spectra contained a strong, narrow band near 3745 cm^{-1} due to ν(O–H) stretching vibrations of isolated terminal silanol groups [12,18,23,47,48]. The asymmetric shape of the terminal silanol peak revealed the presence of SiOH interacting with protons of nearby hydroxyl groups [12,47].

The area of the ν(VO–H) band at 3658 cm^{-1} of the V12 catalyst increased slightly with steam treatment at high temperature, and two new bands appeared around 3696 and 3702 cm^{-1} (part B). Similar observations were previously reported by Berndt et al. [12], who compared the infrared spectra of their VO_x/MCM41 catalyst before and after steaming, and attributed the band at around 3710 cm^{-1} to hydrogen-bonded terminal silanol groups in the walls. Moreover, they explained the increased intensity of the band at 3658 cm^{-1} by the formation of additional V–OH groups due to V–O–Si bridge hydrolysis. A strong enhancement of the ν(VO–H) band was reported by Schraml-Marth et al. [18] after vapor treatment of a dehydrated VO_x/SiO_2 sample at room temperature followed by a heating at 300 °C for 10 min. In the present study, a long evacuation under dry oxygen was required after steam treatment to remove water from the IR cell, leading to possible underestimation of the hydroxylation phenomenon. This hydroxylation can be explained by hydrolysis of V–O–V bridges of oligomeric species or of one of the three V–O–Si bridges of nonhydroxylated monomeric species during the steam treatment.

The observation of bands at around 3700 cm^{-1} on the IR spectrum of the support demonstrates that new silanol groups with a Brønsted acidic character (i.e., weaker O–H bonds) were created during vapor treatment of the pellets. Because the Brönsted acidity of silanol groups interacting with vanadium cations was enhanced [47], the bands observed at around 3700 cm^{-1} could correspond to silanol groups created by V–O–Si bridge hydrolysis. Interestingly, the intensity of the band at 3696 cm^{-1}, observed after only 6 h under O_2 [spectrum (b)], almost disappeared after a longer dehydration time [spectrum (c)]. Therefore, this band could arise from new silanol groups interacting with water molecules via hydrogen bonds.

The spectrum (a) contains also bands around 1630, 1850, and 1960 cm^{-1} (part A), corresponding to combinations modes and overtones of the silica matrix [48]. On both steam-treated V12 catalyst (b) and (c) and support (d) spectra, two new second-order bands at around 1365 and 1420 cm^{-1} appeared. These bands, which could arise from slight structural changes of the silica framework under steam, have not yet been definitively attributed.

The results of Raman and IR spectroscopic studies confirm the dynamic character of vanadium species at the surface of silica. $V_2O_5 \cdot nH_2O$ xerogel, which is stable in ambient air, was completely transformed during thermal treatment. The nature of vanadium species stable at 600 °C seems to strongly depend on properties of the silica, such as the presence of D2 defects observed by Raman spectroscopy. Water vapor is proposed to increase the number of hydroxylated monomeric species present under steam at the reaction temperature and prevent dehydroxylation of silica.

3.3. Specificity of the new VO_x/SiO_2 catalysts by comparison with a catalyst of the same type, V/MCM41

To investigate why the new VO_x/SiO_2 catalysts were more efficient, a comparative study was conducted with a catalyst of the same type, designated V/MCM41, prepared using a protocol described previously [13]. The comparative study involved characterization by TPR, characterization by Raman and IR spectroscopy, and a catalytic test under the same reaction conditions. The catalyst chosen for the comparison was a V16 catalyst with the same V loading as the V/MCM41 catalyst (2.8 wt%).

The dispersion value of the V16 catalyst, deduced from its TPR curve and reported in Table 1, was slightly higher than that of the reference sample prepared by impregnation (85% vs 76%). The Raman spectra of the catalysts after dehydration at 600 °C in air are reported in Fig. 2 below 1100 cm^{-1}. The V16 sample had twice as many silanol group, as deduced from the relative intensity of the ν(Si–OH) band at 970 cm^{-1} (Fig. 2) and the ν(SiO–H) band at 3745 cm^{-1} [7]. However, considering the specific surface areas of the V16 and V/MCM41 samples (980 and 680 $m^2\,g^{-1}$, respectively), their silanol surface concentrations (number of SiOH nm^{-2}) were rather close.

Comparing Figs. 2b and 2c demonstrated an important specificity of the new catalysts. Indeed, the band at 605 cm^{-1} due to D2 defects was much more intense for V16 than for V/MCM41. The neutral pH of the preparation method leading to poorly ordered mesoporous materials could favor the formation of such defects. Another significant particularity was demonstrated by IR spectroscopy. Fig. 6 presents the spectra of the dehydrated V/MCM41 (a) and V16 (b) catalysts and the siliceous support (c). The spectra were normalized relative to the same thickness of dehydrated pellets. The three spectra showed very similar second-order bands between 1400 and 2100 cm^{-1} (not shown). The comparison of the areas of the bands at 3745 cm^{-1} (Figs. 6a and 6b) indicates a greater number of silanol groups in V16 than in V/MCM41, confirming our previous Raman characterization [7]. The band at 3656 cm^{-1} attributed to the ν(OH) stretching vibrations of V–OH bonds was observed for both V16 and V/MCM41; interestingly, the normalized ν(VO–H) peak area of the V16 catalyst was 3.5 times that of the V/MCM41 catalyst. Therefore, both synthesis procedures led to the formation of hydroxylated monomeric vanadium species in the dehydrated state, but our synthesis method allowed a much higher proportion than the impregnation method. By analogy with V-containing zeolites, these species could be stabilized at particular framework or defect sites [49–51].

The catalytic performance of the V16 and V/MCM41 catalysts were determined at 590 °C under the same experimental conditions using the same testing apparatus. The results, reported in Table 2, show that V16 appeared to be twice as active as the reference catalyst and maintained high formaldehyde selectivity; thus, higher productivity was obtained. V16 also was also more active at 570 °C than V/MCM41 at 590 °C with similar selectivity. From the dispersion values (Table 1), the rates of methane conversion per isolated vanadium site can be calculated (Table 2). In view of the values thus obtained, we can conclude that the higher activity of V16 is certainly related to better dispersion of the vanadium species due to the higher specific surface area, but also should be related to the higher intrinsic activity of the isolated vanadium species. Because we found a higher proportion of monomeric hydroxylated vanadium species on the V16 sample than on the V/MCM41 sample, we may postulate that the latter species were more active.

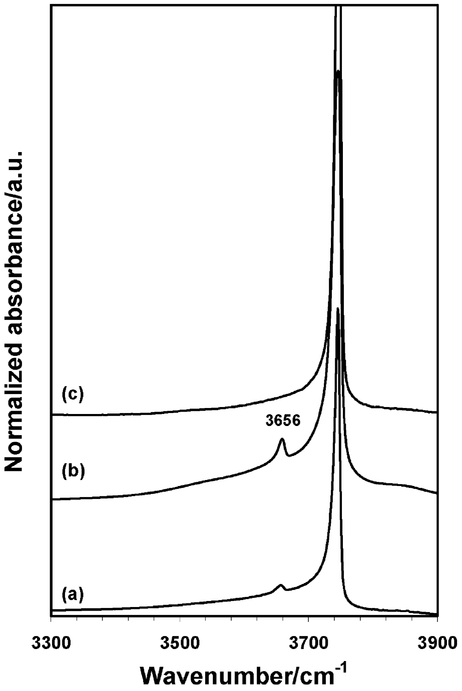

Fig. 6. IR spectra after treatment at 580 °C under flowing O_2 for 12 h of: (a) V/MCM41, (b) V16, and (c) support.

The main difference between the two silica support at the atomic level that could explain the better stabilization of the monomeric hydroxylated vanadium species on V16 than on V/MCM41 is the higher proportion of D2 defects detected by Raman spectroscopy. The new preparation method would allow formation of a poorly ordered support with a higher surface area but also with a high quantity of D2 defects that would have a strong influence on the nature as well as the siliceous environment of active vanadium sites stabilized during thermal activation.

The remaining question concerns the precise nature of the active isolated vanadium species. We recently showed (and have confirmed in the present paper) that efficient catalysts contained isolated vanadium species that were hydroxylated and had one short V=O bond [7]. Such concomitant features have a direct effect on the type of bonding that must exist between

Table 2
Catalytic performances of the V16 and V/MCM41 catalysts

Catalyst	T (°C)	Conversion (%)	Selectivity (%)				Rate	Productivity
			CH_2O	CH_3OH	CO	CO_2	($mol_{(CH_4)}\,mol_{(VO_x\text{-disp})}^{-1}\,s^{-1}$)	($g\,kg^{-1}\,h^{-1}$)
V/MCM41	590	4.6	58	1	39	2	0.101	1500
V16	590	9.2	42	1	54	3	0.181	2200
V16	570	5.4	59	1	38	2	0.106	1800

Feed: 40% N_2/13% O_2/38% CH_4/9% H_2O; GHSV: 109,300 $L\,kg^{-1}\,h^{-1}$.

the V cations and the silica. Taking into account that isolated vanadium species are tetrahedrally coordinated [12,52–54], the number of V–O–Si bonds should be limited to one or two.

A single V–O–Si bond-based model, called the umbrella model, has been proposed [55]. The monomeric silica-supported V species were described as $SiOV{=}O(O_2)$, with a short V=O bond of 0.158 nm and two bonds with a peroxo group. From EXAFS data, the distances to the two oxygen atoms of the adsorbed oxygen molecule and to the oxygen of the support were calculated and appeared to be comparable (0.180 and 0.175 nm, respectively) [56]. This finding was supported by the assignment of the Raman band near 910 cm^{-1} to stretching vibrations of peroxo groups [55,56]. However, we observed a clear increase in the intensity of this band when the temperature was raised to 600 °C in air (Fig. 1). Thus, the previous attribution would lead to the conclusion that peroxo species would be more stable at high temperature. But because this does not seem to be a readily acceptable assumption, we kept our early model based on hydroxylated monomeric species with two V–O–Si bonds that could be described as $(SiO)_2VO(OH)$ species.

Very recently, an alternative umbrella model was proposed in which the vanadium cation had one short V=O bond and two bonds with OH groups [57]. The point group symmetry of the vanadium cation in such a model is C_1 or C_s. In both cases, two ν(VO–H) stretching vibrations would be IR active, but spectroscopic data did not support such a feature. In contrast, only one narrow band at 3658 cm^{-1} was demonstrated by IR spectroscopy. Furthermore, at high temperature and in the absence of water in the equilibrium atmosphere, such species would undergo dehydration, leading to vanadium cations with two V=O short bonds and one V–O–Si bridging bond. However, isotope-exchange experiments have shown that supported vanadium species have only one V=O bond [58,59].

The data presented in this study do not fit with the umbrella models. However, the umbrella models were defined based on experimental data obtained with samples treated at 425–450 °C, whereas in the present study the samples were treated at higher temperature, that is, at the reaction temperature of partial oxidation of methane (550–600 °C). The apparent discrepancies in the results may be due to the heat treatment temperature. The umbrella model would correspond to an intermediate state between the vanadium oxide hydrated at room temperature and the $(SiO)_2VO(OH)$ species observed by Raman spectroscopy at higher temperatures.

4. Conclusion

This study confirms the dynamic character of vanadium species at the surface of silica and allows identification of vanadium species present at the surface of the catalysts at high temperature in the presence of water. Such species, which are believed to be present in the catalytic reaction conditions, correspond to hydroxylated monomeric species.

Based on the characterization results and the comparative study with a conventional V/MCM41 catalyst, we can draw several important conclusions:

(i) The new preparation method leads to a poorly ordered mesoporous support with a high number of silanol groups and D2 defects, which are proposed to favor anchoring of hydroxylated monomeric species during thermal activation. The latter species, present in a higher proportion in the new catalysts, are proposed to be the most active and selective species for methane oxidation to formaldehyde.

(ii) The new method unfortunately allows isolation of only a limited number of vanadium species, as demonstrated by TPR measurements. Furthermore, an increase in the amount of oligomeric species was obtained when the temperature was raised from 400 to 600 °C. These features also could be linked to the properties of the support. Therefore, the design of siliceous support favoring anchoring of a greater amount hydroxylated monomeric species is planned.

(iii) The beneficial effect of adding water vapor to the gas feeds is proposed to be linked to an increase in the number of the active hydroxylated monomeric species. Water may also have an effect in preventing the dehydroxylation of silica.

All of the characterization results presented in the paper and in a previous one [7] lead us to propose that the most active species are hydroxylated monomeric vanadium species, anchored to the support with two V–O–Si bonds. Although both the pyramid and umbrella models cannot be ruled out, they appear to be less likely. In contrast to isolated vanadium species with only one bond to the support (umbrella model), which may be formed indifferently on each Si–OH of the support, the species with two Si–O–V bonds are preferentially anchored at hydrolyzed D2 silica defects. These defects are present in higher proportions in the new catalysts than in ordered mesoporous VO_x/MCM41 catalysts, possibly explaining the better catalytic performance of the new catalysts.

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