Structure and reactivity of sol-gel V/SiO₂ catalysts for the direct conversion of methane to formaldehyde

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Abstract

Vanadium oxide-silica catalysts prepared by the sol-gel method were characterized by different techniques (nitrogen adsorption-desorption isotherms, scanning electron microscopy, X-ray diffraction, temperature-programmed reduction, Raman spectroscopy and X-ray photoelectron spectroscopy) and applied in the direct conversion of methane to C1 oxygenates. The addition of a small amount of nitric oxide to the reaction mixture reduced the energy barrier for H-abstraction, increasing the methane conversion and formaldehyde yield. Correlations between the characterization and activity results indicate that the reaction occurs on tetrahedrally coordinated vanadium sites, as the maximum formaldehyde yield was found for the catalyst with a vanadium content of 1.5 wt%, which has a high surface density of well-dispersed tetrahedrally coordinated monomeric or slightly oligomerized VO₄ species. On the other hand, a high space velocity and CH₄:O₂ ratio decrease the subsequent oxidation to carbon oxides, increasing oxygenate formation.

Keywords: vanadium catalysts, methane/formaldehyde, methane conversion, sol-gel, direct processes

1. Introduction

Methane gas has been identified as one of the most potent greenhouse gases because its global warming effect per molecule is nearly 23 times that of CO₂ on a 100 year timescale [1]. Methane, besides being a greenhouse gas, is also the major constituent of large, underutilized resources of natural gas located in remote areas. In the CH₄ molecule, the C atom has sp³ hybridization, which makes the C-H bond highly stable (439 kJ/mol). Thus, this molecule is reactive only under severe operational conditions [2]. Methane is therefore a promising feedstock for producing value-added products if the problem of C-H activation can be solved.

There are two routes for converting methane to transportable liquid fuels and chemicals, namely, indirect and direct routes. Currently, commercial catalytic technologies are based on the indirect route, which involves a two-step process in which methane is first converted to synthesis gas by steam reforming (Eq. 1) or partial oxidation (Eq. 2), followed by either Fischer-Tropsch synthesis of hydrocarbons (Eq. 3) or methanol synthesis (Eq. 4) and subsequent conversion to oxygenated hydrocarbons.

The direct route is a one-step process in which methane or natural gas is reacted with oxygen or another oxidizing species to give the desired product, e.g., methanol or

formaldehyde (Eq. 5 and Eq. 6). The direct route is regarded to be more energy efficient than the indirect route since it bypasses the energy intensive endothermic steam reforming step of syngas formation.

The catalytic conversion of methane via partial oxidation into transportable liquids, such as methanol and/or formaldehyde, is one direct route for converting natural gas into value-added chemicals. This partial oxidation reaction is one of the greatest challenges in heterogeneous catalysis because the free energy of CO_x formation is higher than that of oxygenates, and consequently, carbon oxides are more easily formed. Moreover, C1 oxygenated products are polar molecules that are easily adsorbed on the catalyst surface and on the reactor wall, which promotes subsequent oxidation to CO or CO₂. It is emphasized that reactor inertness is critically important for obtaining high selectivity for formaldehyde and that even the feed gas should be isolated and not be allowed to make contact with the thermocouple metal wall. Thus, quartz and Pyrex glass-lined reactors have been shown to yield the best results [3].

Currently, CH₃OH and HCHO are produced via a multistep process involving first the conversion of methane to syngas, followed by oxygenate formation in a second step. Although this multi-step process is highly efficient, syngas production is very expensive due to high capital costs and is therefore only economically viable if it is conducted in large-scale plants. A more convenient and economically viable process would be direct methane partial oxidation. It should also be emphasized that methanol, being a precursor to ethylene and propylene, is a primary raw material in the chemical industry [4,5] and formaldehyde is an important precursor in the polymer industry. Thus, the

direct catalytic synthesis of methanol and/or formaldehyde from methane would open the possibility of producing a wide range of important chemicals and fuels.

The direct conversion route involves partial oxidation at 400-650 °C under fuel-rich mixtures to minimize the extent of the more thermodynamically favorable combustion reaction, which produces unwanted CO_x [6-8]. Several recent reviews covering various aspects of the direct partial oxidation of methane to oxygenates have been reported [9-12]. Although the partial oxidation of methane can be conducted (i) non-catalytically in the gas phase, (ii) by heterogeneous catalytic oxidation, (iii) by low-temperature homogeneous oxidation in solution, and (iv) by enzymatic catalytic oxidation, type (i) and (ii) oxidations have been more widely investigated. Gas-phase non-catalytic reactions usually occur via a free radical mechanism at high temperatures, which is unfavorable for controlling the selectivity for the desired oxygenates [5,7]. Thermodynamic and kinetic analyses have shown that the rate-limiting step of the partial oxidation of methane is the first H-abstraction step from the C-H bond to form methyl radicals. Therefore, initiators and sensitizers have been incorporated into the reaction mixture to lower the energy barrier of H-abstraction [6,8]. In particular, nitrogen oxides have been used to promote gas-phase reactions with methane [6,9].

The reactions in Eq. 5 and Eq. 6 also occur on the surface of heterogeneous catalysts. Selective O-insertion into CH₃ or other species obtained from the first H-abstraction of the CH₄ molecule is normally carried out on redox oxides, such as MoO₃ and V₂O₅ [6,9]. In these systems, the catalytic site is an isolated ion (Mo^{δ+} or V^{δ+}) in a slightly reduced state [8-14]. The presence of these partially reduced oxides is believed to allow the redox cycles of catalytic surfaces to proceed more rapidly and smoothly [8]. In addition to the most widely studied silica-supported MoO₃ and V₂O₅ catalysts, many

other metal oxides have also been investigated. Some of them include Ga_2O_3 , Bi_2O_3 [15], Al-doped silica [16] and SbO_x [17].

One of the most used and active catalysts for this reaction is based on silica-supported vanadium oxide [18,19], prepared by incipient-wetness impregnation, as it was found that isolated V^{5+} species were responsible for the active sites. However, despite the great efforts that have been devoted to the development of active and selective catalysts, the product yield for C1 oxygenates still remains poor.

In line with the above state-of-the-art direct conversion of methane to methanol/formaldehyde, we have undertaken this work with the aim to improve the performance of vanadium oxide/silica catalysts by generating essentially isolated V^{5+} ions in tetrahedral coordination with oxide (O^{2-}) ions, which are believed to react in a more selective manner, to therefore obtain better selectivity toward C1 oxygenates [20]. To achieve this objective, a sol-gel methodology was employed to synthesize V/SiO_2 catalysts, and then the resulting catalyst structures were revealed by different characterization techniques, and their influence on the catalytic behavior was examined. This catalyst preparation methodology was chosen because of its simplicity and to achieve a better control of the particle size and morphology of the active phase. Prior to this study, activity tests were carried out to determine the ideal reaction conditions (residence time; methane: oxygen ratio; and addition of a promoter to the feed, such as nitric oxide) that favor the formation of C1 oxygenates.

2. Experimental

2.1. Preparation of silica-supported catalysts

VO_x/SiO_2 catalysts were prepared according to the sol-gel methodology. Tetraethoxysilane (TEOS), $\text{Si}(\text{OC}_2\text{H}_5)_4$, and vanadium acetylacetonate ($\text{V}(\text{acac})_3$) (VAA) were used as precursors. VAA was dissolved in methanol (30 mL methanol/gram of VAA). Then, appropriate volumes of TEOS were selected to obtain 0.2, 0.5, 1.0, 1.5, 2.0, 3.0 and 5.0 wt% vanadium. The resulting transparent green solutions were stirred for 15 min. Then, diluted nitric acid (molar ratio $\text{HNO}_3/\text{TEOS} = 0.7$) was added to the sol for complete hydrolysis and condensation. A thick light green gel was formed within 2 h at ambient temperature. The gel was allowed to age for 1 h and dried at room temperature overnight. Subsequently, the solid was dried at 100 °C for 6 h and finally calcined in static air in two steps: 400 °C for 2 h and 700 °C for 3 h. For the sake of simplicity, the catalysts will be referred to hereafter as xVSi, where x denotes the vanadium weight percent.

2.2. Characterization techniques

Several characterization techniques were used to characterize both the morphology and the structure of the catalysts. These include nitrogen adsorption-desorption isotherms, scanning electron microscopy (SEM), X-ray diffraction (XRD), temperature-programmed reduction (TPR), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

Textural properties were evaluated by N_2 adsorption-desorption isotherms of the samples recorded at liquid nitrogen temperature with a Micromeritics ASAP 2000 apparatus. Samples were degassed at 150 °C under vacuum overnight. Specific areas were calculated by applying the BET method within the relative pressure range $P/P_0 = 0.05$ -0.30. Scanning electron microscopy (SEM) images of the samples were taken with a Hitachi S-3000 N microscope. The samples were metallized with a thin layer of gold

using a Balzers SCD 004 sputter coater. XRD patterns were recorded on a Seifert 3000 powder diffractometer operating with Cu K α radiation ($\lambda = 0.15418$ nm) generated at 40 kV and 40 mA. Scans were recorded at a rate of 0.02°/s for 2 θ diffraction angles between 10° and 90°. Temperature-programmed reduction (TPR) experiments were carried out using a semiautomatic Micromeritics TPD/TPR 2900 apparatus equipped with a TC detector. Prior to reduction experiments, the samples (ca. 30 mg) were thermally treated under air stream at 300 °C to remove moisture. TPR profiles were obtained by heating the samples under a 10% H₂/Ar flow (50 mL/min) from 25 to 800 °C at a linearly programmed rate of 10 °C/min. Raman spectra of the samples were recorded in air using a single monochromator Renishaw inVia 1000 system equipped with a thermoelectrically cooled CCD detector and holographic super-Notch filter. The samples were excited with the 535 nm Ar line. The instrument was internally calibrated with a Si reference at 520 cm⁻¹ and gives a peak position resolution of 1 cm⁻¹, the spectrum acquisition time was 10 s, and 10 spectra were acquired to ensure an optimal signal-to-noise ratio. X-ray photoelectron spectra were recorded on a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer and Mg K α (h.v = 1253.6 eV) X-ray source (12 kV and 10 mA). The powder samples were degassed at 150 °C for 1 h before being transferred into the analysis chamber. Charge effects on the samples were corrected by fixing the binding energies of C1s peak at 284.9 eV due to adventitious carbon. This reference gave binding energy values with an accuracy of ± 0.1 eV. The data were treated with the “XPS peak” software. The spectra were decomposed with the least squares fitting routine using Gaussian/Lorentzian functions after subtracting the Shirley background.

2.3. Activity measurements

The performance of the catalysts in the direct partial oxidation of methane to oxygenates was evaluated in a fixed-bed quartz reactor (4 mm ID, 23 cm length) placed inside a horizontal furnace. The catalyst was placed between quartz wool plugs in the middle of the reactor tube. The temperature of the catalyst bed was measured by a thermocouple located inside a coaxially centered quartz cover. Mixtures of $\text{CH}_4:\text{O}_2 = 2$ (molar ratio) and $150 \text{ mL}_\text{N}/\text{min} \cdot \text{g catalyst}$ ($10 \text{ mL}_\text{N}/\text{min N}_2$) or $2830 \text{ mL}_\text{N}/\text{min} \cdot \text{g catalyst}$ ($40 \text{ mL}/\text{min N}_2$), as well as $\text{CH}_4:\text{O}_2 = 9$ at this last space velocity, were fed into the reactor at atmospheric pressure. In certain reactions, 1 mol% NO was also fed into the reactor, while maintaining the above-mentioned $\text{CH}_4:\text{O}_2$ proportions. Flow rates were adjusted by mass flow controllers, and all gases were mixed prior to reaching the reactor. Effluents from the reactor and feed stream were analyzed by on-line gas chromatography (GC) fitted with a thermal conductivity detector (TCD), using Porapak Q and 4A molecular sieve columns and He as the carrier gas. The outlet of the reactor to the injection port of the GC was heated to 150°C in order to avoid water condensation and formaldehyde polymerization. The initial conditions were 0.55 bar and 50°C for both columns, the Plot-Q and molecular sieve columns, connected in series. Time was adjusted to allow separation of CO_2 in the Plot-Q column in order to avoid CO_2 entering the 5A molecular sieve column, which would lead to saturation of the column. Accordingly, after valve switching, the pressure was raised to 0.8 bar, and CO_2 was eluted. Then, the valve was switched again to allow the separation and elution of H_2 , O_2 , N_2 and CH_4 . A third valve switching avoids vapors entering the molecular sieve column. The temperature was raised to accelerate the elution of water, formaldehyde and methanol. Formaldehyde, CH_2O , has a low signal in TCD, and its presence is masked by baseline disturbances due to the heating ramp. The detection of

formaldehyde is difficult since the detector sensitivity of TCD is low. Formaline was used in order to adjust the method and for calibration, and it was composed of a water solution containing 37 wt% formaldehyde, 10-15 wt% methanol and 53-48 wt% water. The formaldehyde signal is clearer under these conditions, but the TCD sensitivity to formaldehyde is still very low compared to that of water and methanol. This implies that the detection limit for formaldehyde will be low.

3. Results and discussion

3.1. *Characterization of the xVSi catalysts*

Nitrogen adsorption-desorption isotherms of all V-containing catalysts are displayed in Figure 1. These isotherms are of type I+IV, which are assigned to materials with micropores and small mesopores, respectively. The highest proportion of micropores is found for the catalyst with 0.5 wt% vanadium. In addition to this, all isotherms display a very small type H2 hysteresis loop in the range of small mesopores at relative pressures of 0.4-0.6, indicating that the catalysts contain complex micro- and mesoporous networks consisting of pores with ill-defined shapes and a wide pore size distribution. It is worth noting the high values of the BET area for these xVSi catalysts developed by the sol-gel methodology.

The catalysts with higher vanadium content (3VSi and 5VSi) also show a second loop ($P/P_0 = 0.8-1.0$), characteristic of larger sized pores, formed among the vanadium oxide particles [21]. The BET surface areas of catalysts vary between 373 (5VSi) and 589 m^2/g (1.5VSi). From 0.2 wt% V up to 1.5 wt% V, an increase in BET surface area is produced, which is explained by the formation of new mesopores. It can be seen that the

highest BET surface area (1.5VSi) is associated with the largest loop at a P/P_0 of 0.4-0.6. (Figure 1). The increase in surface area by the formation of these mesopores compensates for the loss of area due to the decrease in micropore surface area.

The amount of vanadium atoms per nm^2 was calculated for all catalysts (Table 1). Raman spectroscopy measurements have shown that the monolayer surface coverage of vanadium overlayers on different oxide supports corresponds to approximately 7-8 V atoms/ nm^2 . The maximum monolayer surface coverage without V_2O_5 crystal formation is approximately $0.7 \text{ V}/\text{nm}^2$ for supported V/ SiO_2 catalysts [22]. Comparison with the values of V/nm^2 obtained for the different prepared V-Si catalysts in this study indicates that the formation of crystalline particles of vanadium oxide, using this sol-gel preparation method, is favored when the V content is higher than 3 wt%.

The morphology of the samples was examined by SEM. The SEM images of some representative samples are displayed in Figure 2. The SEM images reveal the presence of agglomerates of irregular shape and are very similar for all samples.

In all these representative samples, large particles with sizes of approximately $100 \mu\text{m}$ are observed, on which finer particles of only a few μm are deposited. The close similarity of the morphology of these particles for all samples indicates that vanadium loading does not alter the large-scale morphology.

X-ray diffraction was used to reveal the presence of crystalline structures in the calcined catalysts. The XRD patterns (Figure 3) present only a broad diffraction at 2θ angles in the range of $10-35^\circ$, which is characteristic of amorphous silica [23]. No diffraction lines belonging to vanadium oxides could be observed. This result indicates that vanadium oxide either forms a highly dispersed phase or the vanadium oxide crystallites

are smaller than the XRD detection limit (2–3 nm). Only the xerogel 5VSi with the highest V loading presents traces of the V_2O_5 phase, which is detected by the observation of tiny peaks at 26.2° , 31.1° and 34.3° . These correspond to the most intense diffraction lines of orthorhombic V_2O_5 (00-01-0359) and do not overlap with the broad diffraction in the range of $10-35^\circ$, characteristic of silica.

TPR experiments were performed to determine the type of vanadium oxide species present on SiO_2 . It should be noted that the SiO_2 substrate exhibited no reduction peak, and therefore it is not reported here for clarity of the figure. The TPR profiles displayed in Figure 4 show that the xVSi catalysts prepared by the sol-gel method exhibit only one reduction peak centered at the temperature range of $505-558^\circ\text{C}$ with a shoulder at higher temperatures. In fact, three different contributions can be detected in the samples shown in Figure 4, (i) m1 at $490-500^\circ\text{C}$, (ii) m2 at $550-560^\circ\text{C}$ and (iii) m3 at $610-620^\circ\text{C}$, which can be, respectively, assigned to the reduction of (i) V_2O_5 -surface species (monomeric or highly dispersed species), (ii) crystalline V_2O_5 (bulk-like V_2O_5 species) to V_6O_{13} species (vanadium (IV,V) oxide) and (iii) the reduction of V_6O_{13} species to V_2O_4 [24,25]. The 0.2VSi sample does not present any reduction peak, which is probably caused by the low V loading, where H_2 consumption during the V-reduction process is below the detection threshold of the equipment.

The maximum of the reduction peak shifts from 505°C for the 0.2VSi catalyst to 558°C for the 5VSi catalyst as a consequence of the reduction process kinetics (effects of the partial pressure of water formed during the reduction and of the actual concentration of the reactant).

The ratio of the area under the reduction curve (m2/m1) for the different catalysts are compiled in Table 2. It can be observed that the proportion of V_2O_5 surface species (m1)

decreased along with the concomitant increase in crystalline V_2O_5 species (m2) with the V loading. For the catalyst with 5 wt% vanadium, compared with the catalysts with 3 wt% vanadium, the increase in the proportion of crystalline V_2O_5 species is very great.

Raman spectroscopy was used to determine the structures present in the catalysts. Raman spectra of the xVSi samples are displayed in Figure 5. The V-free silica substrate showed some features at 487, 607, 802 and 976 cm^{-1} . The 976 cm^{-1} band is associated with the Si-OH stretching mode of surface OH groups. The bands at 802 and $410\text{-}430\text{ cm}^{-1}$ belong to the symmetrical Si-O-Si stretching and bending modes, respectively, while the broad bands at 607 and 487 cm^{-1} are assigned to D2 and D1 defect modes, which have been attributed to tri- and tetra-cyclosiloxane rings produced via the condensation of surface hydroxyls, respectively [26].

The support significantly decreases with increasing vanadium loading, suggesting that the number of three-membered siloxane rings decreases upon dispersion of surface vanadium oxide species. For catalysts with a vanadium amount between 1 and 5 wt%, a band at 1030 cm^{-1} is observed. This Raman shift is related to the stretching vibration of $V=O$. On the other hand, the two bands that appear at 1075 and 915 cm^{-1} are indicative of the formation of V-O-Si bonds. These results reveal that, in addition to the consumption of Si-OH hydroxyls, the deposition of surface vanadium oxide species also breaks some Si-O-Si siloxane bridges to form V-O-Si bridging bonds. When the loading reaches 1.5 wt% V on silica, Raman bands appear at 994, 697, 284 and 144 cm^{-1} , which are due to the formation of crystalline V_2O_5 [27-30]. Thus, the sol-gel methodology to prepare xVSi catalysts was particularly suited to develop isolated $V^{(V)}$ species at vanadium loadings of 1.5-2 wt% V. Catalysts with V loadings higher than this develop a certain proportion of 3D structures, as demonstrated by the Raman spectra of the 3VSi and 5VSi catalysts (Figure 5).

In addition, the nature and concentration of the surface species on all xVSi samples were analyzed by photoelectron spectroscopy (XPS). The V2p core-level spectra of the xVSi catalysts are displayed in Figure 6. The V2p core-level spectra showed the principal V2p_{3/2} peak at a binding energy of 517.7-518.1 eV, which is characteristic of V⁵⁺ species. The fact that the binding energy of the V2p_{3/2} peak shifts slightly from 517.7 eV for the 5.0VSi sample to 518.1 eV for 0.2VSi indicates that V⁵⁺ ions are highly dispersed and interact strongly with the silica network much more when the V loading is lower. Similarly, the O1s spectra were also recorded for all catalysts. For the xVSi catalysts with loadings x = 0.2, 0.5, and 1.0 wt% V, a single symmetric O 1s peak appeared at a binding energy of 532.8 eV, which is characteristic of the Si-O-Si bonds of the substrate. However, for the catalysts with V loadings above 1.0 wt% V, an additional peak with very low intensity ca. 530.3 eV was found, which is characteristic of V-O bonds.

The proportion of vanadium species on the catalyst surface was evaluated from the V/Si atomic ratios and compared with the V/Si nominal ratios (inset of Figure 6). These data indicate that the surface V⁵⁺ content increased linearly with an increase in the total vanadium content, indicating that the vanadium oxide particles are finely dispersed in the silica matrix. The straight line obtained up to a V loading of 2 wt% indicates that V⁵⁺ ions are highly and homogeneously dispersed within the silica matrix. At V loadings above 2 wt%, the V/Si ratios derived from XPS deviate from linearity and are lower than the nominal ratios, indicating that some of the vanadium is segregated toward the surface, forming 3D V₂O₅ nanostructures.

Therefore, these xVSi catalysts prepared by the sol-gel method favor the formation of isolated V⁵⁺ species at V loadings of 2 wt% V or less. Catalysts with V loadings higher than this develop a certain proportion of 3D structures, as demonstrated by the deviation

in the V/Si atomic surface ratio derived from XPS with respect the nominal V/Si ratio (cf, Figure 6, right panel). All these observations show high binding energies of V^{5+} ions in the catalysts with low vanadium loadings and their slight shift to lower binding energies upon increased V loading. This means that V^{5+} ions remain atomically dispersed in the sub-monolayer up to V loadings of around 2 wt%.

3.2. Partial oxidation of methane with the $xVSi$ catalysts

As these reactions are activated, the effect of temperature on the kinetics and selectivity is very important. In previous experiments, the reaction temperature was optimized at 650 °C to increase the yield of C1 oxygenates.

The first activity tests were performed using the 2VSi catalyst, to determine the influence of space velocity, the CH_4/O_2 ratio and the presence of 1 mol% NO in the feed. The obtained results are summarized in Table 3.

From the results compiled in above table, it can be inferred that for the 3 different reaction conditions used, the addition of a small proportion of NO in the feed produces an increase in methane conversion.

It is clear that a high space velocity (comparing the reactions performed with a $CH_4:O_2$ ratio of 2) results in a lower CH_4 conversion, while the HCHO space-time yield follows the opposite trend, greatly increasing both with and without NO in the feed.

Comparison of CO_2 selectivity in both the low and high space velocity reactions verified that a low space velocity enhances the deep oxidation of methane into CO_2 rather than facilitates the partial oxidation reaction of methane into C1 oxygenates. This was interpreted on the basis of the larger residence times of the CH_4 and O_2 reactants and O-containing intermediates within the mesopores of the catalysts, thus facilitating the formation of combustion products.

On the other hand, if the results obtained under high space velocity but with $\text{CH}_4:\text{O}_2$ ratios of 2 and 9 are compared, it can be concluded that, both with and without NO addition, an increased formaldehyde space-time yield is achieved when the higher $\text{CH}_4:\text{O}_2$ ratio is used, though at the expense of a decrease in conversion, which is in accordance with previous results found in the literature [31,32].

In summary, activity measurements with the 2VSi catalyst showed that the best results were obtained by selecting a CH_4/O_2 molar ratio of 9 and a space velocity of 2830 $\text{mL}/\text{min}\cdot\text{g}_{\text{cat}}$. These experimental conditions will be used to compare the performance of the xVSi catalysts in the direct partial oxidation of methane to C1 oxygenates. Such a comparison is very useful in determining the optimum V loading that maximizes catalysts performance.

Prior to testing the xVSi catalysts, the homogeneous reaction for the direct partial oxidation of methane to C1-oxygenates was evaluated without any catalyst in order to study the influence of nitric oxide (NO) addition to the feed stream (1 mol%). As shown in Figures 7 and 8, without NO and in the indicated reaction conditions, no methane conversion is found. When the reaction is performed with the addition of 1 mol% NO, the CH_4+O_2 mixture is converted to a very low extent, with relatively high selectivity for formaldehyde and very low selectivity for carbon monoxide. This is due to the ability of NO to perform the first H-abstraction from CH_4 to generate $\text{CH}_3\cdot$ radicals, which then quickly react with O_2 by forming both peroxy ($\text{CH}_3\text{O}\cdot$) and superoxide ($\text{CH}_3\text{O}_2\cdot$) radicals. These species are the starting points of a complex set of reactions whose final result is the formation of $\text{HCHO}/\text{CH}_3\text{OH}$ and CO_x . The entire process when including $\text{CH}_4+\text{O}_2+\text{NO}$ in the reaction mixture has been modeled, and some conclusions about the kinetics of the slower reactions have been derived [9]. The absence of CH_3OH

in the reaction products under the conditions selected in this work is a result of the high temperature (650 °C) selected.

Figure 7 shows the average HCHO space-time yields obtained in absence of NO in the feed from the homogeneous reaction and from the combined homogeneous and heterogeneous process with the different xVSi catalysts. Moreover, the values obtained under the same experimental conditions but adding 1 mol% NO to the feed stream were included in this figure. It is seen that the V loading has an important effect on the HCHO yield. The HCHO yield initially increases with V loading, reaches a maximum for the 1.5VSi catalyst and then drops at higher V loadings. This occurs in reactions both with and without NO in the feed. It is also seen that the contribution of the homogeneous reaction is important to the entire reaction. The 1.5VSi catalyst also achieves the highest CH₄ conversion (Figure 8). It can be shown that the catalysts with a V content of approximately 2 wt% present the lowest CO₂ selectivity and also that for the 5VSi catalyst (with 5 wt% V loading), a dramatic increase in CO₂ selectivity is produced. The small amount of HCHO formation and the very high selectivity to CO₂ found with the 5VSi catalyst is explained by the presence of relatively large and highly crystalline particles of V₂O₅, which is supported by the different characterization techniques (XRD, N₂ isotherms, Raman spectroscopy, XPS, and reduction profiles), whose results were previously presented and discussed.

The turnover frequency (TOF, mol produced formaldehyde/mol vanadium·second) has been calculated and depicted in figure 7 for reactions with 1% NO in the feed. They represent apparent TOF values, since they are based on the total number of vanadium atoms present in the catalyst. A decreasing trend of turnover frequency from the catalyst with the lowest amount of V up to the counterpart with the highest one is observed. These results support the fact that V loading strongly influences the catalytic behavior,

being the active site for the direct partial oxidation of methane to formaldehyde ascribed to well-dispersed V oxide species.

Correlations between the characterization results and activity tests note that the highest activity for the selective oxidation of methane to C1 oxygenates found for the 1.5VSi catalyst is ascribed to the larger proportion of V-O-Si species on the surface, which are associated with well-dispersed tetrahedrally coordinated monomeric or slightly oligomerized VO₄ species [31-36]. The yield of formaldehyde when using this catalyst is on the order of the most active catalysts based on V-silica found in the literature, e.g., the MCM-41-supported V catalyst [31], but with the advantage of being prepared by a one-pot, single-step and less-expensive sol-gel method.

The surface polymeric V⁵⁺ species contain V-O-V bonds, which are less active for methane conversion than the V-O-Si bonds of the surface monomeric V⁵⁺ species [23]. Thus, for supported VO_x species, in the selective catalytic oxidation of hydrocarbons, with the contribution of many research groups, it has been revealed that the bond that is responsible for catalytic activation is identified as the support-O-V bond [37]. The results reported here show that these surface monomer species are the active sites for methane conversion to C1 oxygenates.

The high dispersion of monomeric (or slightly oligomerized) VO₄ tetrahedral surface species in this catalyst relies on its highest BET surface area, absence or low proportion of crystalline vanadium oxide particles (XRD and Raman), high relative proportion of well-dispersed species on the surface (reduction profile) and linear relationship between the V/Si nominal ratio and its surface V/Si_{XPS} counterpart.

5. Conclusions

From the results reported in this work, the following main conclusions are derived: (i) the xVSi catalysts prepared by a single-step and low-cost sol-gel method showed highly dispersed isolated/slightly oligomerized surface vanadium species up to a vanadium content close to 2 wt%; (ii) up to this V content, the surface V/Si ratios derived from XPS measurements were essentially the same as the nominal V/Si ratios, indicating a uniform distribution of V atoms across the surface; (iii) the formation of 3D V_2O_5 crystalline particles above 2 wt% V was also confirmed by XRD, H_2 -TPR, Raman spectroscopy and N_2 adsorption-desorption isotherms; (iv) 1 % mol NO added to the feed stream enhanced the rate of CH_4 conversion and the partial oxidation to HCHO; (v) a high space velocity and $CH_4:O_2$ ratio promote HCHO formation; and (vi) a maximum HCHO space-time yield amounting to 1610 g HCHO/h·kg_{cat} was found for the catalyst with a vanadium content of 1.5 wt%, which is explained by the higher proportion of V-O-Si species present in isolated VO_4 tetrahedra.

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Table 1. *Textural properties of catalysts*

Catalyst	A_{BET} (m^2/g)	t-plot surface area (m^2/g)	Micropore surface area (m^2/g)	V atoms/ nm^2
Ref.Si	611	575	36 (5.9%)	0
0.2VSi	392	250	142 (36.2%)	0.06
0.5VSi	433	262	171 (39.5%)	0.14
1VSi	476	313	163 (34.2%)	0.25
1.5VSi	589	467	122 (20.7%)	0.30
2VSi	489	341	148 (30.3%)	0.48
3VSi	483	378	105 (21.7%)	0.73
5VSi	373	333	40 (10.7%)	1.58

Table 2. *Ratio between surface and crystalline V_2O_5 species (m2/ml)*

Catalyst	Area m2/Area ml
0.5VSi	0.41
1VSi	0.45
1.5VSi	0.49
2VSi	0.59
3VSi	0.81
5VSi	3.11

Table 3. *Influence of space velocity, CH₄:O₂ ratio and addition of NO to the feed on catalytic performance (catalyst 2VSi)*

Space velocity	150 mLN/min·g catalyst		2830 mLN/min·g catalyst		2830 mLN/min·g catalyst	
CH ₄ :O ₂ molar ratio	2		2		9	
% molar NO feed	0	1	0	1	0	1
Conv CH ₄ (%)	29.2	31.8	4.6	10.2	2.3	3.0
Select. CO (%)	75.3	73.1	60.0	74.1	62.3	59.8
Select. CO ₂ (%)	22.1	23.0	7.8	9.1	4.7	5.7
Select. HCHO (%)	2.7	3.9	32.2	16.8	32.9	34.4
Yield HCHO (g HCHO /h·kg catalyst)	154	220	850	934	874	1112

Figure 1. N_2 adsorption-desorption isotherms of xVSi sol-gel catalysts and the pure SiO_2 reference material.

Figure 2. SEM images of some representative xVSi catalysts.

Figure 3. XRD patterns of support (Ref.Si) and xVSi catalysts.

Figure 4. Reduction profiles of $x\text{VSi}$ catalysts.

Figure 5. Raman spectra of xVSi catalysts with different V-loading.

Figure 6. V2p core level spectra of xVSi catalysts (left panel). Comparison of V/Si atomic ratios derived from XPS with the nominal V/Si ratios (right panel).

Figure 7. CH₂O yield without NO and with 1 vol.% of NO for the xVSi catalyst series and TOF values (mol CH₂O produced / vanadium atom·second) with 1% NO in the feed. Reaction conditions: 650 °C, CH₄/O₂ = 9; GHSV = 2830 mLN/min·g_{cat}.

Figure 8. CH_4 conversion and selectivity to the different products obtained with sol-gel xVSi catalysts. Reaction conditions: 1 vol% NO, GHSV = 2830 mL/min·g_{cat}, $\text{CH}_4:\text{O}_2 = 9$.