Effects of pH and vanadium concentration during the impregnation of Na-SiO₂ supported catalysts for the oxidation of propane

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Abstract: Silica supported sodium vanadate based catalysts have raised interest recently due to reports showing an increase in the selectivity to propene in propane oxidation; a process that may become an alternative to conventional petrochemical routes for producing this valuable olefin. In this work, the effects of pH, the concentration of vanadium in solution, $[V]_{\text{sol}}$, and of their interaction; i.e., non-additive effect, over the properties of Na-SiO₂ (~1.0 wt.% Na distributed as extra- and intra-framework sodium) supported catalysts used for the oxidation of propane under oxygen rich conditions were studied. In general, the studied experimental factors had no net effects over the difference between the nominal and final loadings of vanadium in the catalysts (~10%), the surface area, and porosity. However, all catalysts presented a ~50% decrease in surface area due to partial mesopore blocking reflected by a ~30% increase in the average pore diameter. On the other hand, NaVO₃ microcrystals and particles constituted α -NaVO₃ and β -NaVO₃ phases were formed at acidic pH, whereas sodium metavanadate nanoparticles that had the character of a gel under hydrated conditions were formed at pH=9.0. These nanoparticles transformed into an α -NaVO₃ type phase upon dehydration. The reducibility of the catalysts was a function of the impregnation pH, where the catalysts synthesized at pH=3.8 and 9.0 displayed similar reduction patterns but lower reducibility than the catalyst synthesized at pH=1.5. The produced patterns were correlated to the existence of a mixture of V⁵⁺ and V⁴⁺ species among which V⁴⁺ was prevalent for the catalysts synthesized at pH=3.8 and 9.0. Consequently, the basicity of the catalysts decreased with the increase in pH. The surface concentration of vanadium increased

with the increase in the concentration of vanadium in solution, while the pH had a weak negative effect over the former. On the other hand, it was established that chemical surface state of oxygen in the synthesized catalysts was influenced weakly by the synthesis pH and, more importantly, by non-additive effects between the pH and the concentration of vanadium in solution. The latter was coherent with the detection of surface oxygen species related to the partial dissolution of the Na-SiO₂ support; a phenomenon that seemed to be favored at acidic pH. The latter properties were correlated to changes in basicity. Concerning the catalytic performance, the catalysts synthesized at pH=9.0 displayed the best steady state performance in terms of the selectivity to propene and oxygen consumption. The collected evidence allowed corroborating that both the oxidative dehydrogenation of propane to propene and its combustion to CO and CO₂ are kinetically controlled by the initial activation of one of the C-H bonds of propane. But, the production of CO₂ depended on the level of consumption of O₂; where, a surplus of the latter compared to the conversion of propane combusted the hydrocarbon into CO₂. Such a finding agreed with what has already been established for supported vanadium oxides for hydrocarbon oxidation. An analysis of the Raman spectra of the spent catalysts suggested that under the applied reaction conditions, all catalysts were provided of an active phase mostly constituted by α -NaVO₃ type structures. Therefore, the observed differences in catalytic behavior were rather associated to changes in particle size, reducibility, and acidity

Introduction

The selective oxidation of light hydrocarbons has been studied for almost a century with the first US patents granted to Burke et al. in 1933 and 1934 [1,2]. A first review of the topic was made as early as 1937 by Newitt.[3] Since the beginning, propene was found to be one of the products of the catalytic oxidation of propane. However, researchers only started paying attention to this reaction at the end of the 60s [4–7]. They aimed to increase the production of olefins using processes other than the well-established catalytic dehydrogenation of hydrocarbons. Costs savings in energy and catalyst consumption were since then envisioned because oxidative dehydrogenation reactions are exothermic, and they do not foul the catalyst with coke. Despite such prospects [8,9,18,19,10–17], a commercial process for the oxidative dehydrogenation of propane is not yet a reality.[10,20] The main drawback of oxidative dehydrogenations is their lower thermodynamic favorability when compared to combustion. **Figure S1** plots the standard, $p = 1.0$ bar, Gibbs free energy, ΔG° , as a function of temperature for some of the reactions that can take place in a propane oxidation process made with oxygen. The following reactions were considered: total (i) and partial (ii) combustion, oxidative dehydrogenation (iii), water gas shift -WGS- (iv), and oxidative reforming (v). Reactions (iv) and (v) were included because hydrogen has been reported as a product in some studies [10,21].

Accordingly, oxidative dehydrogenation is only more thermodynamically favorable than the WGS reaction. In addition, to reduce the gap between oxidative dehydrogenation and the combustion and reforming reactions, the process should be run at the lowest temperature possible. Typically, catalysis studies are performed between 400°C and 550°C [8,10,12,13,15,22–24]. In addition, they are normally restricted to conversions of propane around 10% where the production of propene is relatively near to the requirements of a practical application [10,25].

Supported vanadium oxides perform best in the oxidative dehydrogenation of propane.[8,9,26–32] Silica and alumina (mostly γ -Al₂O₃) are archetypical vanadium oxide supports [8,9,36,10,13,28,29,32–35]. The surface chemistry of silica is relatively simpler than that of γ -Al₂O₃ as in regards to the relative distribution of hydroxyls [37,38]. Thus, in principle, this allows a more precise control of the surface distribution of vanadium oxide species over silica. Indeed, Wachs and Weckhuysen[35] pointed out that the formation of isolated surface VO_x units is favored over silica. Isolated VO_x units and other oligomeric two-dimensional vanadium oxide species are considered to favor the production of propene [9,10,13,26,28,31,32,39–41]. However, the strongest limitation for the use of silica as support is its relatively low surface density of hydroxyls, ca. 5 OH/nm², regardless of its surface area [37]. This restricts the loading of vanadium for producing the active phases selective to propene.

The use of sodium for the impregnation of vanadium over silica has been claimed to improve the dispersion of vanadium[42,43] via the formation of oligomeric two-dimensional vanadium oxide species [44–46]. Irusta et al. [42,43] reported this first for catalysts synthesized by the impregnation of ammonium metavanadate - NH₄VO₃- in the presence of NaOH. They suggested the formation of sodium metavanadate, NaVO₃, type compounds. Grant et al.[44,45] found similar trends after impregnating sodium nitrate over SiO₂ and then impregnating vanadium triisopropoxide over the sodium loaded support. On the other hand, Nadjafi et al.[46] showed evidence indicating that SiO₂ supported sodium vanadates may redisperse under the reaction atmosphere of propane oxidative dehydrogenation.

The main variables during the impregnation of a supported catalyst are the pH and the concentration of the metal to be impregnated.[47,48] The effects of these variables on the distribution of vanadium oxides were studied in the past.[34,49] Taouk et al.[49] found that at pH = 4.0 vanadium oxide precipitated over SiO₂ during impregnation, while tetrahedrally coordinated V₄O₁₂⁴⁻ species were prevalent on the catalysts at pH = 11. Deo and Wachs[34] developed predictions for the vanadium oxide structures as a function of these two variables while considering the point of zero charge, PZC, of different oxides supports; namely, MgO, γ -Al₂O₃, ZrO₂, TiO₂, and SiO₂. They used the equilibrium distribution of aqueous vanadium species [50] as a guide. For SiO₂, they predicted that at pH=3.9 and low surface coverage, i.e. for V₂O₅ loadings between 1.5 and 3.0 wt.%, decavanadate-like species, V₁₀O₂₈, are formed while V₂O₅ particles are formed for V₂O₅ loadings higher than 3.0 wt.%. In a further review, Wachs[51] demonstrated that the structure of supported hydrated surface metal oxides was similar to the one found in aqueous solutions if the pH of both the hydrated surface and the aqueous solution was the same. However, the author also warned that cations such as sodium change the structure of the hydrated supported metal oxides. In this sense, as far as the literature reviewed for this paper is concerned, a systematic analysis of the effects of pH and vanadium concentration over the properties of Na-SiO₂ supported vanadium oxide catalysts is still missing.

This work investigates the impregnation of NH₃VO₄ over a 1.0 wt.% sodium loaded silica, Na-SiO₂, support and focuses on how the pH

and the concentration of the vanadium precursor influence the physicochemical and catalytic properties during propane oxidation. The possible non-additive effects[52–54] of these variables over the properties of the catalysts were investigated. The levels of pH and concentration of vanadium were fixed at values where different electrostatic interactions between the dissolved vanadium species and the Na-SiO₂ support occurred,[31] **Figure S2**. The bulk, surface, and catalytic properties of the synthesized materials were analyzed by various techniques and the results were assessed both statistically and phenomenologically.

Results and discussion

The first part of the section refers to the analysis of the bulk vanadium content of the catalysts and to the findings made with SEM-EDS measurements. The second part shows results for the morphology and textural properties of the materials. The third part discusses the chemical structure of the catalysts at the hydrated and dehydrated states. The fourth part discusses the reducibility, basicity, and surface chemistry of the materials. Finally, the catalytic performance is analyzed.

Bulk chemical composition and textural properties. The results of atomic absorption are presented in **Table 1**. In all instances, the deviation of the measured weight percentages of vanadium from the nominal weight percentages of the synthesis was around 10%. The changes of pH did not influence the amount of vanadium deposited over the Na-SiO₂ support.

Table 1. Vanadium loadings, BET specific surface areas, and porosity of the synthesized V(x)-y materials.

Sample	Nominal V wt. %	Difference [%]*	SSA _{BET} [m ² /g]	<PØ>** [nm]
Na-SiO ₂	---	---	18.4±3.51 [#]	10.7±0.6 [#]
V(0.19)-1.5	0.21	9.5	11.2	14.0
V(1.30)-1.5	1.44	9.7	8.7	13.0
V(0.76)-3.8	0.84	9.5	9.9	15.3
V(0.19)-9.0	0.21	9.5	9.4	15.8
V(1.59)-9.0	1.44	10.4	10.3	15.6

Where, y = measured V wt. % and z = pH *Difference = 100×Abs[|(Nominal V wt. % - atomic absorption V wt. %)/Nominal V wt. %|]. [#]Tails of t-Student confidence intervals of 99% and six degrees of freedom. **PØ = average pore diameter as calculated with the BJH method for cylindrical geometry and from the adsorption branch of the isotherm.

Meanwhile, the increase in the concentration of vanadium in the impregnating solution led to an increase in the loading of vanadium in the catalysts. Consequently, catalysts were coded as follows: V(0.19)-1.5, V(1.30)-1.5, V(0.76)-3.8, V(0.19)-9.0, and V(1.59)-9.0. Where, for example, V(0.19)-1.5 is a catalyst whose vanadium loading is 0.19 wt. % and which was impregnated at pH=1.5.

Representative SEM pictures of the Na-SiO₂ support, the catalysts, and bulk vanadium oxide are presented in **Figures 1 and S3**. The support showed a large fraction of broken particles. Their microstructure can be described as a collection of large hemispherical hollow vesicles containing smaller Na-SiO₂ vesicles. On the other hand, almost all the particles of the catalysts were broken. This can be ascribed to their shearing by the magnetic stirrer during the synthesis.

The catalysts synthesized at acidic pH, 1.5 and 3.8, presented microscopic crystals. These microcrystals appeared mixed with the broken husks of the support and, for some regions of the sample, they sprawled from clumps of small particles. The microcrystals formed under conditions other than those typically used for growing crystals with the hydro- and solvothermal methods.[55–57] Furthermore, they did not resemble those of bulk vanadium oxide, **Figure 1**. Basic impurities may directly react with the surface metal oxide species to form nanocrystalline compounds such as CaMoO₄, Na₂MoO₄, and K₂MoO₄. [51] However, no reports on the formation of self-supported microcrystals such as the ones found herein were found. At pH = 1.5, clumps of particles near the microcrystals and microparticles of the broken support were also found. Finally, neither microcrystals nor clumps of small particles were observed for the materials synthesized under a basic pH, 9.0; indeed, only broken particles were seen in the micrographs.

EDS analysis of a sample of 12 particles from the support, **Figure S3**, allowed establishing that their composition can be represented by the empirical formula: Na_{0.024±0.002}SiO_{1.554±0.102} (the formula was calculated considering a t-Student 95% confidence interval for the media with 11 degrees of freedom, and excluding carbon). Thus, the support did not have the composition for stoichiometric SiO₂.

Concerning the catalysts, SEM-EDS analysis of the structures found for V(1.30)-1.5 allowed identifying their chemical composition, **Figure S3**. Accordingly, the microcrystals examined with EDS for V(1.30)-1.5 were rich in vanadium; median mole% ~17.2, and poor in silicon, median mole% ~8.0. EDS data also showed the presence of aluminum as an impurity of the microcrystals, median mole% ~0.3. The origin of this impurity could be the NH₄VO₃ salt used for the synthesis[58] or traces of aluminum in the Na-SiO₂ support itself. Using the median as a metric to represent the composition of the sampled microcrystals, the following empirical formula was deduced taking vanadium as a calculation basis: (Al_{0.02}Si_{0.47})Na_{0.56}VO_{3.61}; which hints to the formation of sodium metavanadate microcrystals. On the other hand, the clumps of particles showed a more heterogeneous composition with maxima for silicon and aluminum mole% of ca. 18.3 and 9.8, respectively, while the concentration of vanadium was ca. 5.1 mole%. Two of the EDS examined clumps had a median empirical formula: (Si_{0.34})Na_{0.42}VO_{2.20}, which was similar to the empirical formula of the microcrystals but without the aluminum impurity. Therefore, some of the observed clumps were made of sodium metavanadate structures. A precise identification of the crystalline structure of the sodium vanadate structures identified by SEM-EDS was not possible by XRD, nonetheless see Supplementary Information and **Figure S4** for details. Finally, the microparticles associated with the broken support were the most rich in silicon, median mole% ~32.2, and the most poor in vanadium, median mole% ~1.2, and with a median empirical formula, using silicon as a basis, corresponding to (Na_{0.04}V_{0.04})SiO_{2.01}. Therefore, these particles were mostly composed of the Na-SiO₂ support with vanadium dispersed over them.

The examination by EDS of the particles of V(0.76)-3.8 suggested the existence of a mixture of vanadium oxides and sodium metavanadates; namely, the following empirical formulas were obtained: (Al_{0.02}Si_{0.33})Na_{0.01}VO_{0.33} and (Al_{0.18}Si_{0.66})Na_{0.43}VO_{1.90}.

Figure 1. Selected scanning electron micrographs for samples of the synthesized materials and bulk vanadium oxide for reference. For SEM analyses, the samples were directly introduced to the instrument from the ambient. Nomenclature: V(x)-y. Where, x = vanadium loading, wt.%, and y = impregnation pH.

Results also showed the presence of particles mostly composed of silica; median empirical formula: $\text{SiO}_{1.50}$, with some of them showing traces of sodium and vanadium, **Figure S3**. Finally, the samples from V(1.59)-9.0 were always rich in silicon and their median empirical formula was: $(\text{Na}_{0.02}\text{V}_{0.02})\text{SiO}_{1.60}$. As already mentioned, no discernible vanadium structures were found for this material by SEM. Therefore, it can be deduced that vanadium was best dispersed in the catalysts synthesized at pH = 9.0 as compared to the other catalysts.

Figure 2 shows the N_2 physisorption isotherms and the BJH pore size distribution and accumulative pore volume for a sample of the Na-SiO₂ support **(a)** and for a sample of V(1.59)-9.0 **(b)**. Representative isotherms for the other catalysts can be found in **Figure S5**. In general, both the support and the catalysts showed the same kind of isotherm with unrestricted adsorption at the limit $P/P_0 \sim 1.0$ and a very wide hysteresis loop closing at $P/P_0 \sim 0.6$. This type of isotherm does not make part of the IUPAC system.[59,60] Adamson proposed that they should be classified as isotherms for solids which are not fully wetted by the adsorbate.[61] Barby, as cited by Rouquerol et al.[62], found similar isotherms for silica xerogels and proposed that they are due to voids of ca. 10 nm between spherical particles. The latter matches the BJH estimation of the average pore size of the Na-SiO₂ support studied herein. Concerning the hysteresis loop, it seems to be a mixture of the types H2(b); found for systems where pore blocking effects are present, and H3; which are associated to either non-rigid aggregates of plate-like particles or to a pore network made of macropores which were not filled with liquid N_2 .[59] Considering the above literature and SEM observations, the pore network of the materials studied herein may consist of interparticle voids making a mesoporous network connected to larger cavities that make a macropore network.

Table 1 shows the BET surface area of the materials. The fulfillment of the Rouquerol consistency criteria is shown in **Table S1**. Repeated measurements of the Na-SiO₂ support allowed establishing that its media BET surface area was $18.4 \pm 3.5 \text{ m}^2/\text{g}$ ($t_{\alpha=0.01}$; $v = 5$), whereas the ensemble of the measured supported

catalysts had the media: $9.9 \pm 3.5 \text{ m}^2/\text{g}$ ($t_{\alpha=0.01}$; $v = 4$) which implies that, regardless of the synthesis conditions, the catalysts had ~50% less BET surface area than the Na-SiO₂ support. Further application of equation (S1) led to a media for the normalized BET area, N_{SSABET} , within the interval 0.604 ± 0.008 ($t_{\alpha=0.01}$; $v = 4$), which indicates that there were vanadium structures

blocking mesopores.[63] BJH calculations for estimating the pore size distributions of the materials, **Figure 2** and **Table 1**, further supported the latter hypothesis. Indeed, the media for the average pore diameter of the catalysts was larger, $14.7 \pm 2.2 \text{ nm}$ ($t_{\alpha=0.01}$; $v = 4$) than the one of the Na-SiO₂ support; $10.7 \pm 0.6 \text{ nm}$ ($t_{\alpha=0.01}$; $v = 5$), which suggests that the smaller mesopores were blocked by the impregnation of vanadium.

Figure 2. Representative N_2 physisorption isotherms and BJH pore size distributions, assuming cylindrical geometry, and cumulative pore volume for samples of (a) Na-SiO₂ and (b) V(1.59)-9.0.

Chemical structure of the hydrated catalysts. Raman characterization of selected samples of fresh Na-SiO₂ (reference, dehydrated state), V(1.30)-1.5, V(0.76)-3.8, and V(1.59)-9.0 in the hydrated state are shown in **Figure 3**. The supplementary information features additional Raman spectra for hydrated samples of the catalysts: V(0.19)-1.5 and V(0.19)-9.0, **Figure S6a**.

In general, Raman measurements over different regions of the catalysts, **Figure S6b**, showed that vanadium species were heterogeneously distributed over the support. This finding coincided with SEM-EDS results presented earlier. Furthermore, the Raman spectra found for the Na-SiO₂ supported vanadium

catalysts differed from those recorded for a VO_x/SiO_2 benchmark and for bulk V_2O_5 , **Figure S6c**.

For Na-SiO_2 , broad peaks and shoulders at 52, 94, 296, 408, 456, 488, 603, 741, 787, 832, 937, and 1030 cm^{-1} were observed. The spectrum found showed bands that have been reported for both vitreous and commercial silicas.[64–73] Concerning vitreous silicas; i.e. those thermally treated at $T \geq 1100^\circ\text{C}$, Ivanda et al. reported a very broad band in the region $50 - 200\text{ cm}^{-1}$ ascribed to a Boson peak.[65] Richet et al.[74] showed that this peak is generated by the libration of SiO_4 tetrahedra. It can be noticed that the Boson peak is not present for samples of conventional silica supports.[66–71] The band at 1030 cm^{-1} for Na-SiO_2 can also be ascribed to SiO_4 tetrahedron (T_d symmetry), but in this case the band for the material studied herein was blue shifted in regards to the literature.[72] A shortening of the Si-O bonds of the tetrahedra could be responsible for the blue shift.[71] Such a shortening will be later shown to be associated to the presence of $\equiv\text{Si-O-Na}^+$ structures in which sodium replaces silicon in the silica framework. A second very wide peak for vitreous silica appears between 200 and 700 cm^{-1} . This feature was attributed to bond bending.[65] Gao et al.[71] proposed that the Raman bands recorded at 408 cm^{-1} are due to the symmetrical Si-O-Si stretching mode. In addition, the peaks found in the region between 740 to 840 cm^{-1} could be due to the Si-O-Si bending mode.[71] Within the region between 400 and 600 cm^{-1} , the peaks at 488 and 603 cm^{-1} are ascribed to the so-called D2 and D1 defect modes associated to tri- and tetracyclosiloxane rings produced via the condensation of surface hydroxyls.[64,65,71] On the other hand, the band at 937 cm^{-1} could be considered to be a red shift of the band at 970 cm^{-1} which is ascribed to the stretching vibration of surface Si-(OH) bonds.[71,72] Considering the effects reported for alkali metals on this kind of bonds,[72] this red shift could be considered to be due to an enlargement of the Si-(OH) bond by the presence of extra-framework sodium in $\equiv\text{Si-O-Si-O}^--\text{Na}^+$ structures, as it will be shown later.

Figure 3. Raman spectra for selected samples of hydrated V(1.30)-1.5, V(0.76)-3.8, and V(1.59)-9.0, and for a sample of dehydrated Na-SiO_2 , for reference purposes. Nomenclature: V(x)-y. Where, x = nominal vanadium loading, mol.%, and y = impregnation pH.

The Raman spectrum for the sample from V(1.30)-1.5, **Figure 3**, shows four consecutive peaks whose intensity decreased as follows: $952 > 917 > 943 \geq 910\text{ cm}^{-1}$. This family of peaks matched those ascribed to antisymmetric νVO_2 ($900 - 920\text{ cm}^{-1}$) and symmetric νVO_2 ($940 - 956\text{ cm}^{-1}$) vibrations in bulk $\alpha\text{-NaVO}_3$ and $\beta\text{-NaVO}_3$ crystals.[75,76] The peaks at 511 and 546 cm^{-1} could be ascribed to symmetric $\nu\text{V-O-V}$ vibrations while the peak at 640 cm^{-1} may be due to the antisymmetric $\nu\text{V-O-V}$ vibration of the same $\alpha\text{-NaVO}_3$ structure.[75,76] The peaks at 349 and 369 cm^{-1} matched those assigned to δVO_2 units in $\alpha\text{-NaVO}_3$. Meanwhile, the four peaks whose intensity decreased in the order $245 > 254 > 222 \geq 180\text{ cm}^{-1}$ belong to different V-O-V vibrations such as: $\delta\text{V-O-V}$, ρ_r , ρ_t , ρ_w , and chain deformations.[75–77] Finally, the peaks at 63 and 95 cm^{-1} belong to lattice modes of either $\alpha\text{-NaVO}_3$ or SiO_4 tetrahedra, respectively [74–76].

The Raman spectrum for hydrated V(0.76)-3.8, **Figure 3**, mostly coincided with the pattern for bulk $\beta\text{-NaVO}_3$ with traces of $\alpha\text{-NaVO}_3$. Among the bands recorded for this material, five subsequent bands whose intensity decreased in the order $945 > 952 \geq 887 > 917 > 925\text{ cm}^{-1}$ were found. Comparing them with those found for V(1.30)-1.5, the band at 945 cm^{-1} was the strongest for V(0.76)-3.8 while it was one of the weaker for V(1.30)-1.5. Also, the intensity of the band at 952 cm^{-1} decreased for V(0.76)-3.8 as compared to the same band for V(1.30)-1.5. Finally, the band at 887 cm^{-1} was not observed for V(1.30)-1.5. This pattern conforms to the β -phase of bulk NaVO_3 whose stronger bands are at 888 and 945 cm^{-1} . [75,76] Furthermore, the strong bands observed at 200 , 431 , and 739 cm^{-1} and the weaker ones at 138 , 173 , 291 , 297 , and 925 cm^{-1} are also distinctive of bulk $\beta\text{-NaVO}_3$ as compared to $\alpha\text{-NaVO}_3$. Meanwhile, as discussed before, the bands at 254 , 512 , 643 , 917 , and 952 cm^{-1} are characteristic of $\alpha\text{-NaVO}_3$ hence suggesting that the catalyst V(0.76)-3.8 is composed of a mixture of α - and $\beta\text{-NaVO}_3$. Finally, the band at 1050 cm^{-1} may be associated to the vibration of terminal V=O vanadyls stemming from either monomeric or oligomeric VO_4 species.[9,26,80,81,28,35,36,42,46,69,78,79] According to Wachs, [51] four coordinated VO_4 units are charge balanced by sodium in structures such as polymeric metavanadates, $\text{Na}_n(\text{VO}_3)_n$, dimeric pyrovanadates, $\text{Na}_4\text{V}_2\text{O}_7$, and isolated orthovanadate, Na_3VO_4 .

According to the above results, the synthesis conditions applied herein led to the formation of two distinct bulk sodium metavanadate crystalline phases; namely, α - and $\beta\text{-NaVO}_3$. This behavior is particular because while $\alpha\text{-NaVO}_3$ is a thermodynamically stable phase, $\beta\text{-NaVO}_3$ is metastable[82,83] hence it is supposed to irreversibly transform into $\alpha\text{-NaVO}_3$ when calcined from 405°C . [75,82] However, recent results from Nadjafi et al.[46,84] have shown that silica supported catalysts composed of mixtures of vanadium oxide and sodium vanadate phases also contain the metastable $\beta\text{-NaVO}_3$ phase. Where, the stabilization of $\beta\text{-NaVO}_3$ may be due to its interaction with $\text{Na}_{1+x}\text{V}_3\text{O}_8$ and VO_x species dispersed over the silica support.

The change between the Raman spectra for the hydrated catalysts synthesized at acidic pH and those synthesized at basic pH was rather drastic. Indeed, the sample from V(1.59)-9.0 showed wide and often poorly defined peaks at 59 , 95 , 488 , 740 , 940 , and 1040 cm^{-1} that resembled those found for the Na-SiO_2 support. Overall,

the pattern of the Raman spectrum and SEM-EDS results for V(1.59)-9.0 suggested that vanadium species were present on this type of catalyst either as an amorphous or nanocrystalline phase. Among the peaks of weak intensity that did not appear in the spectrum of the Na-SiO₂ support were those at 178, 261, 323, 387, 431, 470, 611, 809, 888, and 915 cm⁻¹. Among these, the ones at 888 and 915 cm⁻¹ and the feature at 940 cm⁻¹ were also found in the Raman spectrum of V(0.76)-3.8. Also, as already discussed, the peaks observed between 170 and 500 cm⁻¹ originate from V-O-V and VO₂ vibrations. Such findings suggested the presence of sodium metavanadate phases (α - and β - phases or some other intermediate phases [44,46,82–84]) for this catalyst. One may wonder whether the recorded spectrum can be ascribed to a sodium orthovanadate, Na₃VO₄, type structure since similar Raman patterns to the one observed in **Figure 3** have been previously associated to this type of compound [42]. However, the Raman spectrum reported by Sigma-Aldrich [85] for bulk Na₃VO₄ does not resemble the spectrum found herein. Therefore, the presence of Na₃VO₄ was discarded. On the other hand, one unintended consequence of synthesizing the catalysts at basic pH is the potential partial dissolution of the support. Particularly, because the dissolution of silica at basic pH is kinetically favored by alkali ions.[86] This process is known to occur by the breakage of surface $\equiv\text{Si-O-Si}\equiv$ bonds that may react with hydroxyl ions to produce adducts of silicic acid, H₂SiO₄²⁻, which are in equilibrium with H₃SiO₄⁻. [86–88] As discussed earlier, silicas show peaks at 488 and 603 cm⁻¹ that are ascribed to defects.[64,65,71] Stolen et al.[72] showed that the intensity of these bands increases with the concentration of OH hydroxyls. For V(1.59)-9.0, the increase in the intensity of the bands at 488 and 611 cm⁻¹ may hence be due to an

Figure 4. UV-vis-DRS spectra for selected samples of hydrated V(1.30)-1.5, V(0.76)-3.8, and V(1.59)-9.0. The signal for sample V(1.59)-9.0 and its decomposition has been multiplied by 2, to get a better resolution of the entire spectra. Nomenclature: V(x)-y. Where, x =nominal vanadium loading, mol.%, and y = impregnation pH.

increase in the relative concentrations of the D2 and D1 defects, respectively. Particularly, the peak at 611 cm⁻¹ would correspond to a red shift of the D1 defect implying a lengthening of the bond associated to this defect.

UV-vis-DRS examination of the hydrated catalysts is shown in **Figure 4**. In general, the spectra from the catalysts synthesized at acidic pH had low intensity. Conversely, the spectra for the catalyst synthesized at basic pH was intense as in agreement with the formation of dispersed sodium vanadates. The edge energies of the hydrated samples increased in the order: V(0.76)-3.8 (Eg ~ 5.10 eV) $\approx$ V(1.30)-1.5 (Eg ~ 4.99 eV) > V(1.59)-9.0 (Eg ~ 3.15 eV). On the one hand, the edge energies for V(1.30)-1.5 and V(0.76)-3.8 differed from the values reported for pure sodium vanadates; namely, 3.28 eV for NaVO₃ and 4.17 eV for Na₃VO₄. [89] Therefore, the UV-vis-DRS recorded for the hydrated catalysts synthesized at an acidic pH did not correspond to those expected for bulk sodium vanadates or to other vanadates (e.g. Eg-AlVO₄ = 3.14, Eg-KVO₃ = 3.09, etc.[89]). This finding can be explained by the fact that these materials consisted of self-supported microcrystals and clumps of sodium vanadate particles sparingly dispersed over the Na-SiO₂ support. Indeed, the edge energy for SiO₂ is 5.79 eV [89] which is a value closer to the one found for the samples of the catalysts synthesized at acidic pH. Also, Catana et al.[90] reported an UV-vis-DRS for silica which shows the same features as the ones found for V(1.30)-1.5 and V(0.76)-3.8. Therefore, the UV-vis-DRS spectra for these catalysts was strongly influenced by the one of the Na-SiO₂ support and their interpretation for identifying vanadium species would be doubtful.

On the other hand, the edge energy for hydrated V(1.59)-9.0 was very close to that reported for bulk NaVO₃ [89]. In addition, the high intensity of the spectrum for V(1.59)-9.0 was a sign of a higher concentration of more homogeneously distributed vanadium species [91]. Considering that the value of the edge energy for V(1.59)-9.0 was ~ 3.15 eV, it is likely that the dominant species for this type of catalyst consists of sodium vanadates whose structure could be similar to that of dimeric pyrovanadates Na₄V₂O₇ [51,71]. Edge energies within the range 3.0 to 3.2 eV are distinctive of polymeric VO₄ units [71]. The deconvolution of the UV-vis-DRS spectrum for V(1.59)-9.0 allowed identifying bands at ~1.8, ~2.7, ~3.2, ~4.3, and ~5.0 eV, **Figure 4**. These bands coincided with the UV-vis-DRS spectra for supported vanadium oxide type catalysts shows several bands in the region between 1.5 and 6.5 eV (850 – 190 nm).[33,71,77,90–92] Thus, the bands at ~1.8 eV were ascribed to d-d absorption bands for O $\rightarrow$ V^{+IV} transitions [77,90,91]. The bands at ~2.7 and ~3.2 eV can be attributed to 2D-square pyramidal or 3D-octahedrally coordinated (group Oh) bulk-like VO_x units [77,91]. Finally, the bands at ~4.3 and ~5.0 eV were ascribed to tetrahedrally coordinated VO_x species (Td symmetry group) [91].

Chemical structure of the dehydrated catalysts. **Figure 5** shows Raman spectra for samples from dehydrated V(1.30)-1.5, V(0.76)-3.8, and V(1.59)-9.0. Raman spectra for samples of the other synthesized catalysts are found in **Figure S6**. Dehydration brought changes for the Raman spectra of the catalysts.

For V(1.30)-1.5, a strong contribution at 1066 cm⁻¹ was found. This contribution can be related to isolated vanadyl species from the sodium vanadates or from (SiO)₃V=O structures [9,26,78–81,93,94,28,35,36,42,46,51,69,71].

Figure 5. Raman spectra for selected samples of dehydrated V(1.30)-1.5, V(0.76)-3.8, and V(1.59)-9.0. Nomenclature: V(x)-y. Where, x = nominal vanadium loading, mol.%, and y = impregnation pH.

In the latter case, the band around 927 cm^{-1} may also be associated either to the formation of bridging V-O-Si bonds from $(\text{SiO}_4)_2(\text{VO}_3)_2$ structures [71,81,93–95]. Another explanation for the band at 927 cm^{-1} is that, as discussed earlier, it is due to the vibration of V-O-V bonds from the self-supported $\beta\text{-NaVO}_3$ crystals. In this sense, the bands at 131, 293, 433, 557, 740, and 877 cm^{-1} can also be associated to $\beta\text{-NaVO}_3$ since they were also found for the hydrated samples of V(0.76)-3.8. These bands added to the ones already characterized as belonging to the $\alpha\text{-NaVO}_3$ phase, **Figure 3**. Thus, the proposal of an interconversion between the $\alpha\text{-NaVO}_3$ and $\beta\text{-NaVO}_3$ phases found further support.

The spectrum from dehydrated V(0.76)-3.8, **Figure 5**, kept most of the peaks found for its hydrated counterpart, **Figure 3**, while losing the bands at 643 and 952 cm^{-1} which were associated to the $\alpha\text{-NaVO}_3$ phase. Although a band at 1066 cm^{-1} was also found for dehydrated V(0.76)-3.8, its intensity was very weak as compared to the same band found for V(1.30)-1.5. Therefore, the contribution of this kind of species to the chemical composition of the dehydrated V(0.76)-3.8 catalyst was very low.

The dehydration of V(1.59)-9.0 allowed establishing that, in this state, the material is composed of similar sodium vanadate phases as the ones found for the catalysts synthesized at acidic pH. Particularly, the recorded spectrum showed well defined Raman peaks whose intensity decreased in the order: $949 > 944 > 508 > 917 > 635 > 288 > 124\text{ cm}^{-1}$ plus some clearly discernible shoulders at 104, 151, 244, 316, 471, 557, 741, and 892 cm^{-1} . Following this evidence, the sodium vanadates in the catalyst V(1.59)-9.0 were more prone to be structurally modified by hydration. According to Gao et al.,[71] hydrated vanadium oxides molecularly resemble more $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gels than V_2O_5 crystals. The structure of such a gel would be constituted by chain and/or 2D polymers made of highly distorted square pyramidal VO_5 units connected by V-OH-V bridges stabilized by the formation of hydrogen bonds of the type $\text{Si-OH} \cdots \text{V}$. [71] In addition, the $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gel has regions where the V-O-V bonds may hydrolyze to form O-V-(OH)_3 species able to

migrate over the surface of silica.[96] One may suppose that this kind of behavior is shared by the supported sodium metavanadates studied herein as well hence explaining the marked differences between the Raman spectra for the hydrated and dehydrated V(1.59)-9.0.

H₂ reduction profiles of the catalysts. **Figure 6** shows the hydrogen temperature reduction profiles for samples of the catalysts V(1.30)-1.5, V(0.76)-3.8, and V(1.59)-9.0, bulk vanadium oxide, and for the VO_x/SiO_2 benchmark. The TPR pattern of the benchmark showed a peak centered at 628°C and shoulders at 695 and 761°C . According to the literature,[97–99] the first peak corresponds to the reduction of V^{5+} species to VO_2 (V^{4+}), while the latter shoulder is associated with further reduction to V_2O_3 (V^{3+}). The reduction patterns of the V(1.30)-1.5, V(0.76)-3.8, and V(1.59)-9.0 were more complex as compared to the one found for the benchmark. The reduction of V(1.30)-1.5 started around 350°C and showed its maximum at 424°C . Afterwards, a feature appeared at 601°C followed by a last sharp peak at 701°C and a shoulder at $\sim 810^\circ\text{C}$. The reduction process stopped at 900°C where the H_2O signal returned to its baseline. Accordingly, the reduction of V(1.30)-1.5 started earlier and finished later than the reduction of the benchmark. This trend agrees with literature reports[100,101] in which the addition of alkalis decreased the temperature at which vanadium oxides start to reduce. Such a behavior has been attributed to the formation of bronze-like phases in which the V^{4+} oxidation state is stabilized.[100] Tentatively, the shift to lower reduction temperatures may be explained when considering that the sodium cation attracts the electron cloud from one of the oxygens of the metavanadate structure hence enlarging the bond distance between the vanadium center and the oxygen linked to sodium. The latter consideration may also partly explain the very broad reduction pattern recorded for V(1.30)-1.5.

V(0.76)-3.8 started reducing at $\sim 390^\circ\text{C}$ and its pattern included one summit centered at 665°C , two lower intensity peaks at 440 and 550 , and a shoulder at 805°C . If the reduction sequence $\text{V}^{5+} \rightarrow \text{V}^{4+} \rightarrow \text{V}^{3+}$ is assumed to take place, one may thus say that most of the vanadium was present as V^{4+} for this catalyst. On the other hand, the reduction peaks at 550 and 665°C had an approximately constant shift of $\sim 50^\circ\text{C}$ to lower temperatures in regards to the peaks at 601 and 701°C from V(1.30)-1.5.

The reduction pattern for V(1.59)-9.0 was very similar to the one found for V(0.76)-3.8. But, the summit and the lower temperature shoulders of the profile for V(1.59)-9.0 were shifted $\sim 30^\circ\text{C}$ higher as compared to the same features for V(0.76)-3.8. Some authors,[102,103] have shown that larger supported vanadium oxide structures are harder to reduce as compared to smaller ones. However, this latter explanation did not coincide with the tendencies found for the SiO_2 supported sodium vanadate phases presented herein. Indeed, an estimation of the consumption of H_2 during TPR experiments, please see methodology in the Supplementary Information, showed that H_2 consumption decreased with the size of the vanadium structures according to the following: bulk V_2O_5 ($23.29\text{ }\mu\text{mol H}_2/\text{g}$) > V(1.30)-1.5 ($1.72\text{ }\mu\text{mol H}_2/\text{g}$) > V(0.76)-3.8 ($0.96\text{ }\mu\text{mol H}_2/\text{g}$) > VO_x/SiO_2 benchmark ($0.90\text{ }\mu\text{mol H}_2$) > V(1.59)-9.0 ($0.80\text{ }\mu\text{mol H}_2/\text{g}$). Hence, instead of the explanation presented in the literature,[102,103] it seems that the

Figure 6. TPR profiles for selected samples of V(1.30)-1.5, V(0.76)-3.8, V(1.59)-9.0, bulk V_2O_5 , and VO_x/SiO_2 benchmark. Nomenclature: V(x)-y. Where, x = nominal vanadium loading, mol.%, and y = impregnation pH.

reducibility of the current supported sodium vanadates could be rather associated to the aforementioned stabilization of V^{4+} species by sodium cations which agrees with the already discussed Raman results for the dehydrated catalysts.

Considering the above, the recorded temperature programmed profiles allowed to conclude that: (1) the supported sodium vanadate catalysts started reducing at lower temperatures than the VO_x/SiO_2 benchmark and the bulk V_2O_5 ; and, (2) The catalysts V(0.76)-3.8 and V(1.59)-9.0 had lower reducibility than the V(1.30)-1.5 catalyst. This trend was correlated to the size of the sodium vanadate structures which was lower for the former.

Surface chemical state of the catalysts. The description of the surface chemical state of the catalysts comprises the elemental composition and distribution of chemical species as measured with

X-ray photoelectron spectroscopy, the dispersion of exposed vanadium sites as estimated from O_2 chemisorption experiments, and the basicity of the catalysts assessed by the temperature programmed desorption of CO_2 .

Surface chemical composition. The quantification made from the spectra recorded for the Na- SiO_2 support is shown in **Table S2**. Accordingly, the media empirical formula of the surface of the support was $(C_{0.068 \pm 0.020})Na_{0.040 \pm 0.002}SiO_{1.763 \pm 0.036}$ ($t_{\alpha=0.05, \nu=5}$) which was roughly similar to the one found with SEM-EDS. It must be noted that the binding energy scale of all the spectra was calibrated with the Si 2p peak set at 103.52 eV for the reasons explained in the Supplementary Information, **Figure S7**. **Table S3** shows the quantification made for all the samples measured for each one of the catalysts. Empirical formulas describing the composition of the surface of the catalysts were derived from these results are presented in **Table 2**.

The formulas showed that the surface of the catalysts V(0.19)-1.5, V(0.19)-9.0, and V(0.76)-3.8, was enriched by sodium. Overall, the stoichiometry of the surface of the catalysts V(1.30)-1.5 and V(1.59)-9.0 was closer to the one of $NaVO_3$ as compared to the other catalysts. On the other hand, **Figure S8** shows that the samples taken from the first and second replicates of the catalyst V(1.30)-1.5 showed two N 1s peaks at average positions ~ 401.8 and ~ 407.8 eV, **Figure S8f** and **S8g**, respectively, while a sample from the second replicate of the catalyst V(0.76)-3.8, **Figure S8k**, displayed a single N 1s peak at 408.12 eV. The peak at ~ 401.8 eV was ascribed to N^{1+} atoms in $ONOO^-$ moieties, while the peaks ~ 408 eV are ascribed to N^{5+} atoms in NO_3^- anions.[104]

Table 2. XPS average relative molar ratios for the synthesized V(x)-y catalysts, normalized to the concentration of silicon, and empirical formulas thus deduced. Nomenclature: V(x)-y.

Catalyst	Molar ratios					Derived formula
	C	Na	O	Si	V	
V(0.19)-1.5	0.097	0.056 2.631	1.853	1.000	0.021 1.000	$\{C_{0.097}\}-(Na_{2.631}V)_{0.021}[SiO_{1.853}]$
V(1.30)-1.5 [§]	0.147	0.032 0.362	1.945	1.000	0.088 1.000	$\{C_{0.147}\}-(Na_{0.362}V)_{0.088}[SiO_{1.945}]$
V(0.76)-3.8 [§]	0.075	0.053 2.311	1.811	1.000	0.023 1.000	$\{C_{0.075}\}-(Na_{2.311}V)_{0.023}[SiO_{1.811}]$
V(0.19)-9.0	0.046	0.053 4.707	1.793	1.000	0.011 1.000	$\{C_{0.046}\}-(Na_{4.707}V)_{0.011}[SiO_{1.793}]$
V(1.59)-9.0	0.132	0.051 1.124	1.795	1.000	0.046 1.000	$\{C_{0.132}\}-(Na_{1.124}V)_{0.046}[SiO_{1.795}]$

Where, x = nominal vanadium loading, mol.%, and y = impregnation pH. [§]Traces of nitrogen were found for samples from some of the replica of these catalysts, see **Table S3**.

According to **Table S3**, the surface concentration of nitrogen in these catalysts were 1.05, 0.76, and 0.31 mol% for V(1.30)-1.5 replicate 1, V(1.30)-1.5 replicate 2, and V(0.76)-3.8 replicate 2, respectively. Therefore, in the case of V(0.76)-3.8 replicate 2, the surface of the sample contained 0.31 mol% of NO_3^- anions, while

the surface of V(1.30)-1.5 replicate 1 and V(1.30)-1.5 replicate 2 contained 0.45 and 0.36 mol% of NO_3^- anions, respectively. Finally, the surface concentration of $ONOO^-$ moieties for the latter two samples were 0.60 and 0.40 mol%, respectively. These results confirmed the proposal of one of the reviewers of this paper that

residual NaNO_3 and parent ONOO^- moieties were present at the surface of the catalysts when the synthesis was made at acidic pH.

Figure 7 features main effects and interaction plots for statistically assessing the effects of the factors studied during the synthesis of the catalysts over the surface concentration of vanadium. Accordingly, the pH and the concentration of vanadium in the impregnating solution had weak (i.e., the averages of the XPS surface concentration of vanadium at each experimental level were very near to the limits of a 95% t-Student confidence interval for the global mean of the data) negative and positive effects, respectively, over the surface concentration of vanadium.

Figure 7. Main effects, a) and b), and interaction, c) and d), plots for assessing the effects of pH and concentration of vanadium in the impregnating solution – $[\text{V}]_{\text{sol}}$ – over the XPS surface concentration of vanadium for the synthesized $\text{V}(\text{x})$ -y catalysts.

On the other hand, the interaction plots for the pH and the concentration of vanadium in the impregnating solution showed parallel lines hence ruling out non-additive effects over the output variable. A supplementary analysis of how impregnation pH and vanadium solution concentration influenced the concentration of exposed vanadium was made from the data collected during O_2 chemisorption experiments, **Figure S9** (raw data are found in **Table S4**). The results of this analysis basically coincided with those made with XPS, but the positive effect of the concentration of vanadium in solution over the concentration of exposed vanadium measured by O_2 chemisorption appeared stronger. Finally, comparing the surface concentration of vanadium of the sodium vanadate-based catalysts with the one measured for the VO_x/SiO_2 benchmark, **Table S3**, no evidence about an increase in the dispersion of vanadium due to sodium was found.

Concerning the distribution of surface chemical species, **Figures 8 to 10** are statistical plots for analyzing the binding energies displayed by the Na 1s, O 1s, and V $2p_{3/2}$ core lines of the spectra recorded for the samples of the catalysts. **Figure S8** shows the decomposition of each one of the recorded high resolution spectra from which **Figures 8 to 10** were made. In the case of the Na 1s core line, only the concentration of vanadium in solution produced a significant effect over the position of the peak, **Figure 8b**. The highest concentration of vanadium in solution led to a shift of the

Na 1s core line of ~ -0.4 eV; i.e., the average binding energy for Na 1s core line for the catalysts synthesized with the highest concentration of vanadium in solution was ~ 1073.2 eV. A negative shift in the position of an XPS core line is interpreted as an increase in the reduction state (or vice versa a decrease in the oxidation state) of the element. Therefore, these results suggested that increasing the concentration of vanadium in the impregnation solution led to surface sodium vanadate species where sodium was more reduced. In this sense, Kishi et al.[105] showed that lower concentrations of sodium over an oxidized $\text{V}/\text{Cu}(100)$ surface resulted in more reduced sodium species.

According to the plots done for the position of the summit of the O 1s core line, **Figure 9**, neither the pH nor the concentration of vanadium had statistical effects that overcame the 95% confidence limit threshold. However, a negative correlation between the O 1s binding energy and pH was found in the main effect plot of pH. This suggested that pH had a weak effect over the position of the O 1s core level; namely, increasing pH led to more reduced oxygen species.

Figure 8. Main effects, a) and b), and interaction, c) and d), plots for assessing the effects of pH and concentration of vanadium in the impregnating solution – $[\text{V}]_{\text{sol}}$ – over the position of the Na 1s core line of the $\text{V}(\text{x})$ -y catalysts. Nomenclature: $\text{V}(\text{x})$ -y. Where, x = nominal vanadium loading, mol.%, and y = impregnation pH.

In addition, the cross-over found for the interaction plots, **Figures 9c** and **9d**, indicated the existence of an interaction effect. In this case, the interaction was synergistic for the $[\text{V}]_{\text{sol}} \times \text{pH}$ plot and antagonistic for the $\text{pH} \times [\text{V}]_{\text{sol}}$ plot[52] which implied that its origin was related to factors other than the input variables of the experiment. Therefore, a closer examination of the components of the O 1s core line for all the studied materials was made. **Table S5** summarizes the binding energies and full widths at half maximum (FWHM) of the components considered for the decomposition of the O 1s peak from the samples of the Na- SiO_2 support (**Figure S10**) and the $\text{V}(\text{x})$ -y catalysts (**Figure S8**).

Figure 9. Main effects, a) and b), and interaction, c) and d), plots for assessing the effects of pH and concentration of vanadium in the impregnating solution – $[V]_{\text{sol}}$ – over the position of the summit of the O 1s core line of the $V(x)$ -y catalysts. Nomenclature: $V(x)$ -y. Where, x = nominal vanadium loading, mol.%, and y = impregnation pH.

The characteristics of the surface of the support before impregnation will be assessed first. **Figure S10** shows the recorded high resolution spectra for the support. Except for one sample, the average position of the O 1s peak was 533.63 ± 0.04 eV ($0.04 = \text{standard error} = \text{standard deviation} / \sqrt{\text{number of data}}$) with an average FWHM = 2.09 ± 0.05 eV. Similar parameters have been reported for silica samples.[106,107] Therefore, the component marked as O 1s-II in **Table S5** can be ascribed to oxygen in a $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bond; which is called bridging oxygen.[108] For the sample which showed two components, Na-SiO₂-3, the first component appeared at 531.40 eV and the second at 533.07 eV. The presence of these two components was accompanied by the detection of two components for the Si 2p core level as well, **Figure S10b**; namely, one for the $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bond at 103.52 eV and another at 102.16 eV for a chemical species in which the silicon atom would be more reduced. Also, for this sample, the peak for the Na 1s core level showed two components; one at 1071.52 eV, FWHM = 2.65 eV, and another at 1073.04 eV, FWHM = 2.06 eV. These results suggested the existence of two surface structures. The first one was assigned to a sodium silicate type structure and it was associated to the peaks of Si 2p, O 1s, and Na 1s at 102.16, 531.26, and 1071.52 eV, respectively. Such an assignment agreed with the proposal made by Mekki et al.[108] These authors explained that in sodium silicates Na₂O breaks up the SiO₄ tetrahedra hence producing $\equiv\text{Si}-\text{O}^--\text{Na}^+$ moieties for which the oxygen is called non-bridging. In this case, the lower binding energies of the Si 2p, O 1s, and Na 1s peaks is coherent with the fact that the %ionic character of the $\equiv\text{Si}-\text{O}$ bond in a $\equiv\text{Si}-\text{O}^--\text{Na}^+$ structure is lower than in SiO₂. [106] On the other hand, the Na 1s component at 1073.04 eV was ascribed to an extra-framework exchangeable species[109] bonded to surface dehydroxylated moieties as in $\equiv\text{Si}-\text{O}-\text{Si}-\text{O}^--\text{Na}^+$ abducts. The presence of the aforementioned species was coherent with the Raman analyses made earlier for the support, **Figure 3**, but, the fact that they only appeared in one of the six

samples analyzed by XPS suggested that the surface of the support was dominated by $\equiv\text{Si}-\text{O}-\text{Si}-\text{O}^--\text{Na}^+$.

Several samples from the catalysts; namely, samples one and five from $V(0.19)$ -1.5, two and three from $V(0.76)$ -3.8, sample one from $V(0.19)$ -9.0, and sample 3 from $V(1.59)$ -9.0, **Table S5**, showed high resolution spectra for the O 1s core line with only one component belonging to the $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bridging oxygen species. The spectra from the Si 2p and Na 1s core lines for these samples, **Figures S8a, S8e, S8k – S8m**, and **S8r** were also similar to the ones found for the support in which only $\equiv\text{Si}-\text{O}-\text{Si}-\text{O}^--\text{Na}^+$ species were found, **Figures S10a – S10b, S10d – S10f**.

For several samples of the catalysts, a third oxygen component was identified at an average binding energy of 534.43 ± 0.16 eV, **Table S5**. The literature ascribes high binding energy O 1s components to surface hydroxyls, to adsorbed water,[110,111] and to oxygen linked to carbon (i.e., organic oxygen).[112,113]

Organic oxygen may be neglected in the case of the samples analyzed herein because of their very low concentration of adventitious carbon. Indeed, the contribution of carbon oxides to the C 1s core line of adventitious carbon is roughly 30% of its total concentration at most,[112] which for the current samples may make ~ 1.05 mol.% in average. The latter is a rather negligible contribution to the oxygen concentration whose average was around 60% in all instances, **Table S3**. Therefore, the high energy components recorded for some of the samples of the catalysts might be rather associated to surface hydroxyls or adsorbed water. It is known that silica dissolves over both acidic and basic aqueous solutions,[87,114–117] and this leads to the apparition of high binding energy peaks for oxygen.[118] The dissolution of silica is kinetically faster under basic pH than under acidic conditions, though.[116] Therefore, it was somehow unexpected to find that the high binding energy peak for oxygen was mostly present for the catalysts synthesized at acidic pH, **Table S5**. Indeed, among the catalysts synthesized at basic pH, the high binding energy component of the oxygen peak was only found for samples of the $V(0.19)$ -9.0 catalyst. This led to hypothesize that an increase in the concentration of vanadium can slow the dissolution of silica under basic conditions. Such a hypothesis was reasonable because it has been shown that, for example, aluminum can suppress the dissolution of silica under basic pH conditions.[119]

Conversely, from the current results, **Table S5**, it seems that vanadium may help accelerate the dissolution of silica under acidic conditions. This can be explained by the fact that NH_4VO_3 forms vanadic acid, HVO_3 , under acid pH.[57,120] A compound that in combination with sodium cations attack the silica framework of zeolites.[121–123]

Concerning the O 1s components found at the lowest binding energy, the third sample from $V(0.19)$ -1.5, all the samples from $V(1.30)$ -1.5, and all except one sample from $V(1.59)$ -9.0 showed an oxygen component at a binding energy interval between 530.47 and 531.33 eV. Among these samples, two out of those examined for $V(1.30)$ -1.5 displayed clearly separated components around 530.57 ± 0.02 eV. The third sample for both $V(0.19)$ -1.5 and $V(1.30)$ -1.5 as well as one of the samples from $V(1.59)$ -9.0 showed a

shoulder at 530.70, 530.47, and 530.72 eV, respectively. The results for these five samples were separated into two groups; one where the low binding energy component had an average binding energy of 530.54 ± 0.04 eV which corresponded to samples from V(1.30)-1.5, and another where this component was found at an average binding energy of 530.71 ± 0.01 eV for samples of V(0.19)-1.5 and V(1.59)-9.0. The stoichiometry between the oxygen component at 530.54 ± 0.04 eV and the total concentration of vanadium was $\text{VO}_{1.23 \pm 0.22}$. Meanwhile, the stoichiometry between the oxygen component at 530.71 ± 0.01 eV and vanadium was $\text{VO}_{2.11 \pm 0.01}$. Therefore, there was consistency in considering two distinct oxygen species at the lowest binding energy for the above series of samples. On the other hand, one sample from V(1.30)-1.5 and three from V(1.59)-9.0 showed the lowest binding energy O 1s component as a shoulder at 531.24 ± 0.04 eV. The stoichiometry of this component in relation to vanadium was $\text{VO}_{1.97 \pm 0.52}$, hence it was close to the stoichiometry of the already analyzed oxygen component at 530.71 ± 0.01 eV. However, the component at 531.24 ± 0.04 eV overlapped with the component ascribed to non-bridging oxygen, $\equiv\text{Si}-\text{O}^--\text{Na}^+$. Therefore, it was not possible to separate both these contributions.

In what follows, a characterization of the V 2p core line is made. **Figure 10** assesses the statistical effects of the studied experimental factors over the position of the V 2p_{3/2} core level. In general, only the concentration of vanadium in solution had a statistical effect over the binding energy of the V 2p_{3/2} core level. More precisely, the increase in the concentration of vanadium led to a monotonous decrease in binding energy from ~ 518.3 to 517.7 eV; i.e., the increase in the concentration of vanadium in the impregnating solution led to more reduced vanadium species.

It was not possible to find a systematic study on the XPS characterization of silica supported sodium vanadates in the literature.

Figure 10. Main effects, a) and b), and interaction, c) and d), plots for assessing the effects of pH and concentration of vanadium in the impregnating solution – [V]_{sol} – over the position of the V 2p_{3/2} core line of the V(x)-y catalysts. Nomenclature: V(x)-y. Where, x = nominal vanadium loading, mol.%, and y = impregnation pH.

A comparison of the binding energies measured in this work with those reported for bulk vanadium oxides, bulk NaVO_3 , and silica supported vanadium oxides yields useful information, though. In this sense, careful and detailed XPS studies made for bulk vanadium oxides[124–126] show that there is an average ~ 1.0 eV difference between V^{5+} and V^{4+} species in bulk vanadium oxides, where the V 2p_{3/2} core line for the former typically shows binding energies around ~ 517.5 eV whereas the latter appears at ~ 516.0 eV. On the other hand, bulk NaVO_3 [127] and bulk Na_3VO_4 [128] typically show the V 2p_{3/2} core line at ~ 517.5 eV hence implying that vanadium is as V^{5+} in sodium vanadates as well. Therefore, it seems safe to conclude that the binding energies of the V 2p_{3/2} core line recorded for the catalysts studied herein mostly correspond to V^{5+} species associated with the chemical structures studied earlier in the paper.

Particular attention was brought to the fact that several catalysts displayed V 2p_{3/2} peaks at binding energies around and higher than 518 eV, **Figures 10** and **S8**. Some authors have found similar results for supported vanadium oxide catalysts and have proposed that such a tendency is due to highly dispersed vanadium species.[129,130] Such a proposal was tested by plotting the recorded V 2p_{3/2} binding energies as a function of the surface concentration of vanadium, **Figure S11**. The latter assumption was reasonable since the concentration of vanadium measured by XPS was linearly correlated to the concentration of exposed vanadium measured during O_2 chemisorption experiments, **Figure S12**.

The tendency observed in **Figure S11** led to reject the hypothesis that the binding energies higher than 518 eV recorded for the V 2p_{3/2} peak were due to an increase in dispersion because there was an inverse dependency of the binding energy on the concentration of surface vanadium.

An alternative interpretation of the high binding energies found some of the V 2p_{3/2} peaks can be postulated considering that an increase in binding energy in XPS implies a decrease in the electron density around the assessed element. As a consequence, the peaks at higher binding energies for vanadium have a higher Lewis acidic character than those at lower binding energies.[131] Therefore, it was considered that the V 2p_{3/2} peaks with binding energies higher than 518 eV corresponded to more acidic vanadium species. Further correlation of the surface Na/V molar ratios of the catalysts with the binding energy of the V 2p_{3/2} peak, **Figure S13**, provided support for this proposal since the Na/V molar ratio had a positive effect on the binding energy of the V 2p_{3/2} peak.

Basicity of the catalysts. **Figure 11** presents the results for CO_2 temperature desorption tests made for representative samples of the catalysts V(1.30)-1.5, V(0.76)-3.8, and V(1.59)-9.0. The recorded profiles showed the following: (i) the total basicity of the catalysts decreased as follows: V(1.30)-1.5 ($0.32 \mu\text{mol CO}_2/\text{g}$) > V(0.76)-3.8 ($0.25 \mu\text{mol CO}_2/\text{g}$) > V(1.59)-9.0 ($0.09 \mu\text{mol CO}_2/\text{g}$). (ii) V(1.30)-1.5 had both weak; CO_2 desorption peak at 142°C , and strong basic sites; with a CO_2 desorption region showing a shoulder at 460°C , a sharp peak summit at $\sim 530^\circ\text{C}$, and a final shoulder at 585°C . (iii) V(0.76)-3.8 only had strong basic sites with a broad desorption region with three summits at 412, 500, and 585°C . Where, the latter was the sharpest peak. (iv) V(1.59)-9.0 had the

poorest basicity with the least intense CO_2 signal. The catalyst showed a very broad desorption region at low temperature (up to $\sim 150^\circ\text{C}$) and another very broad desorption region with broad peaks at 460 and 585°C .

The above tendencies showed the influence of the impregnation pH over the basicity of the catalysts; namely, the total basicity of the catalysts decreased with increasing pH and the relative distribution of basic sites was also modified by pH. These effects can be related to the differences in chemical structure of the catalysts discussed in the previous sections. Indeed, one may recall that the chemical structure of the catalysts synthesized at acidic pH, V(x)-1.5 and V(0.76)-3.8, mostly consisted on microcrystalline sodium vanadate structures while at basic pH particles of sodium vanadates were formed. Furthermore, the XPS analysis made earlier showed that the surface of the catalysts impregnated at basic pH was populated by more acidic species.

Figure 11. CO_2 temperature desorption profiles for representative samples of the catalysts. Nomenclature: V(x)-y. Where, x = nominal vanadium loading, mol.%, and y = impregnation pH.

Catalytic reactivity of the materials. First, the evolution of the fractional conversion of propane and the products yields will be presented and discussed as a function of time on stream and reaction temperature. Second, the dependency of selectivity with propane conversion will be analyzed. Third, an analysis of the functionalities of the catalysts considering their chemical structure will be done.

Figure 12 shows the evolution of the conversions (X_i) and products yields (y_j) as a function of time on stream for the oxidation of propane over representative samples of the synthesized catalysts. The behavior of the silica support and of the other replicates of the catalysts is found in **Figure S14**. In general, both the conversions of propane and oxygen were below 0.15 for the V(x)-y catalysts. Therefore, it was considered that the reactor was operated in a differential mode.

The stability of the catalysts was analyzed by statistically comparing (t-Student test) conversions at 450°C before and after ramping the reaction temperature to 500°C . In this sense, the catalyst V(1.30)-1.5 was stable, $p\text{-value}(\text{XC}_3\text{H}_8) = 0.63$ and $p\text{-value}(\text{XO}_2) = 0.50$, **Table S6**. This behavior contrasted with the one found for V(0.76)-3.8 and V(1.59)-9.0 whose performance at 450°C before and after ramping up to 500°C changed; namely, for V(0.76)-3.8, $p\text{-value}(\text{XC}_3\text{H}_8) = 0.04$ and $p\text{-value}(\text{XO}_2) = 0.03$, and for V(1.59)-9.0, $p\text{-value}(\text{XC}_3\text{H}_8) = 1.83 \times 10^{-8}$ and $p\text{-value}(\text{XO}_2) = 7.01 \times 10^{-13}$.

In addition, the results in **Figure 12** showed that: (i) the conversion of the reactants over V(1.59)-9.0 increased after ramping down the temperature; $\text{XC}_3\text{H}_8 = 0.012 \pm 0.002$ and $\text{XO}_2 = 0.005 \pm 0.001$ for 450°C up and $\text{XC}_3\text{H}_8 = 0.044 \pm 0.002$ and $\text{XO}_2 = 0.036 \pm 0.001$ for 450°C down, while those for the V(0.76)-3.8 decreased; $\text{XC}_3\text{H}_8 = 0.011 \pm 0.001$ and $\text{XO}_2 = 0.012 \pm 0.001$ for 450°C up and $\text{XC}_3\text{H}_8 = 0.007 \pm 0.002$ and $\text{XO}_2 = 0.010 \pm 0.000$ for 450°C down. (ii) At 500°C , there was a strong positive gap between the conversions of O_2 and C_3H_8 for V(0.76)-3.8 (average steady state $\text{XO}_2 = 0.111 \pm 0.002$ and $\text{XC}_3\text{H}_8 = 0.070 \pm 0.001$), and basically no gap between them two for V(1.59)-9.0 (average steady state $\text{XO}_2 = 0.111 \pm 0.001$ and $\text{XC}_3\text{H}_8 = 0.100 \pm 0.001$).

Figure 12. Evolution of reactants fractional conversion and products fractional yields as a function of time on stream and temperature for representative samples of the synthesized catalysts. Reaction conditions: propane GHSV = 4 h^{-1} , feed composition = 5:10:115 [mL NTP /min] $\text{C}_3\text{H}_8:\text{O}_2:\text{N}_2$, p = atmospheric pressure (Bucaramanga $\sim 0.89 \text{ bar}$). Nomenclature: V(x)-y. Where, x = nominal vanadium loading, mol.%, and y = impregnation pH.

Further comparison between the performance of the sodium vanadate based catalysts and the VO_x/SiO_2 benchmark, **Figure S15**, showed that the latter was more active than the sodium

vanadate based catalysts, compare **Figures 12** and **S15**. The transient behavior at 500°C found for V(0.76)-3.8 and V(1.59)-9.0 was not found for the VO_x/SiO_2 benchmark, nonetheless. Up to 400°C, the benchmark showed a conversion of C_3H_8 that was above the conversion of O_2 (average steady state $XC_3H_8 = 0.030 \pm 0.001$ and $XO_2 = 0.010 \pm 0.001$ at 400°C), **Figure S15a**; this was the same kind of behavior observed for the V(1.30)-1.5 catalyst, **Figure 12**. At 450°C, the conversions of both C_3H_8 and O_2 became the same for the benchmark (average steady state $XC_3H_8 = 0.049 \pm 0.001$ and $XO_2 = 0.048 \pm 0.001$), whereas at 500°C there was a strong increase in both conversions; where, the conversion of O_2 showed the strongest increase under non-steady state conditions and then reached more than the double of the conversion of C_3H_8 at steady state (average steady state $XC_3H_8 = 0.126 \pm 0.003$ and $XO_2 = 0.309 \pm 0.002$). Comparing these results to those found for V(1.59)-9.0, **Figure 12**, it was noticed that both the benchmark and V(1.59)-9.0 showed similar levels of C_3H_8 conversion at steady state, but the consumption of O_2 by V(1.59)-9.0 was ca. thrice lower.

The above findings suggested that the initial sodium vanadate phases of the catalysts evolved differently during the catalytic tests. Specifically, there would have not being an evolution of the active phase of the catalyst synthesized at pH=1.5 regardless of the changes in temperature. Meanwhile, the active phases of the catalysts synthesized at pH=3.8 and pH=9.0 would have evolved at 500°C with time on stream under the reaction atmosphere. To investigate this above hypothesis, Raman analysis of the spent catalysts in their dehydrated state was carried out and it is shown in **Figure 13**. In the case of V(1.29)-1.5, the spectrum of the spent catalyst did not show the contribution of vanadyl band at 1066 cm^{-1} .

Figure 13. Raman spectra for selected samples of dehydrated V(1.30)-1.5, V(0.76)-3.8, and V(1.59)-9.0 after reaction (dotted spectra correspond to spectra before reaction and that were included for comparison purposes). Nomenclature: V(x)-y. Where, x = nominal vanadium loading, mol.%, and y = impregnation pH.

Apart from this, the recorded spectrum was basically the same that was recorded for the fresh dehydrated catalyst though with some changes in the relative intensity of the Raman bands. This latter trend coincided with the fact that the behavior of V(1.29)-1.5 during

the oxidation of propane did not evolve with time on stream and that there was no difference between the results recorded at the different reaction temperatures before and after ramping up and down the temperature of the reactor. The fact that this catalyst was stable despite the absence of the original band corresponding to vanadyls for the sample of the spent catalyst suggests that these species played no significant role on the catalytic behavior under the studied reaction conditions. Indeed, some literature reports show that vanadyl bonds may not have an effect on the catalytic behavior of supported vanadium oxides.[26,28,35,69,79,94]

For V(0.76)-3.8, new Raman bands at 920 and 954 cm^{-1} were observed for the sample of the spent catalyst, **Figure 13**.

These bands hinted a modification of the chemical structure of the catalyst during the reaction; which agrees with the evolution of the catalytic performance with time on stream. As discussed before, the bands that appeared in the spectrum for spent V(0.76)-3.8 are associated to $\alpha\text{-NaVO}_3$. Therefore, the formation of such phases would be favored for this catalyst under the studied reaction environment.

Finally, for V(1.59)-9.0, no new Raman bands were observed when comparing the spectra for the dehydrated catalyst in its fresh and spent state, **Figures 5** and **13**.

In general, **Table 3** summarizes the evolution of the chemical structure of the catalysts as characterized by Raman and UV-DRS. Therefore, the observed evolution of the activity with time on stream for V(1.59)-9.0, **Figure 12**, may not be associated to a modification of the chemical nature of the active phase of the catalyst under the reaction environment. An alternative explanation for the behavior observed for this catalyst is related to the possible presence of a combination of low temperature reactant adsorption effects and to diffusion and thermal effects [132–134].

In this sense, V(1.59)-9.0 displayed what is called a normal hysteresis behavior; i.e., the conversion of reactants was higher after ramping down the temperature of the reactor, **Figure 12**. When analyzing hysteresis, the ramping up branch of the reaction temperature is called the ignition (or light-off) process while the temperature ramping down branch of the sequence is called the extinction (or light-out) process.[135] During ignition, the catalyst reaches a temperature; the ignition or light-off temperature, where a sudden and strong increase in reactants conversion happens. In the case of the oxidation of hydrocarbons such as methane and propene, there is evidence[136,137] that hysteresis may be associated to the formation of surface carbonaceous sites that form from the dissociative adsorption of the hydrocarbon and to the enrichment of the surface of the catalyst by chemisorbed oxygen. However, the Raman spectra recorded for spent catalysts, **Figure 13**, did not support this explanation. On the other hand, the most traditional explanation of the hysteresis phenomenon is that ignition leads to overheating of the active sites of the catalysts which can neither be quenched by the gaseous stream passing through the reactor nor can it be sensed by the thermocouple in contact with the catalytic bed.[132] If this is the case, the strength of the hysteresis phenomenon should depend on the conversion of the hydrocarbon. A comparison between the hysteresis curves for a sample from one of the replicates of the V(1.59)-9.0 catalyst and the VO_x/SiO_2 benchmark, **Figure S16**, suggested that this may be

the case for the benchmark whose conversion of both propane and oxygen was allowed to reach higher levels during testing. Meanwhile, if this was the effect determining the increase in conversion for V(1.59)-9.0 its impact was rather weak.

Table 3. Evolution of the chemical structure of the sodium vanadate phases of the catalysts as characterized by Raman and UV-DRS.

Catalyst	State		
	Hydrated	Dehydrated	Spent
	Applied thermal treatment		
	Calcination, dry air 500°C. Regular storage: exposition to ambient.	Calcination 300°C, storage in sealed bags with silica desiccant	Recovered after propane oxidation tests ($O_2/C_3H_8=2.0$). Dehydrated
Detected vanadate phases			
V(1.30)-1.5	α - $NaVO_3$ majority; β - $NaVO_3$, minority.	β - $NaVO_3$, ($\equiv Si-O$)- $V=O$.	β - $NaVO_3$
V(0.76)-3.8	β - $NaVO_3$, majority. α - $NaVO_3$ minority.	β - $NaVO_3$.	α - $NaVO_3/\beta$ - $NaVO_3$
V(1.59)-9.0	$NaVO_3$ type phases; e.g., $Na_4V_2O_7$, "gel state"	α - $NaVO_3/\beta$ - $NaVO_3$	α - $NaVO_3/\beta$ - $NaVO_3$

Considering the above evidence, the following can be concluded: (1) the active phase of the catalysts synthesized at pH=1.5 mostly corresponded to α - $NaVO_3$ structures belonging to bulk self-supported microcrystals which were chemically stable under the studied reaction environment. However, the performance of this material was the poorest among the synthesized catalysts. (2) When pH=3.8, i.e., the chemical structures that were present at the beginning of the reaction were mostly of the β - $NaVO_3$ type (dehydrated catalysts, **Figure 5**) and evolved into an active phase related to α - $NaVO_3$. (3) When pH=9.0, the active phase of the catalyst was also ascribed to the formation of a α - $NaVO_3$ type phase whose chemical structure did not seem to evolve with time on stream during the catalytic tests, **Figure 5**. Although, its catalytic performance positively evolved towards a higher activity which did not sacrifice propene selectivity.

Overall, the catalyst synthesized at pH=9.0 performed best in the reaction of oxidation of propane in terms of both stability and consumption of propane and oxygen. Regarding the latter, its consumption in oxidative dehydrogenation reaction is seldom discussed in the literature despite its importance for a potential commercialization the process [8,10]. On the other hand, during the revision of the manuscript, one of the reviewers suggested that the lower performance of the catalysts synthesized at acidic pH could be related to a deleterious effect of surface $NaNO_3$ and $ONOO^-$ moieties detected by XPS. However, the results featured herein did not allow confirming this proposal. Furthermore, it was not possible to find any literature report on the effects of these species over propane oxidation.

Concerning the distribution of products, CO_2 was the main reaction product for all catalysts, and its yield was followed by the ones to C_3H_6 and CO , **Figure 12**. Water was also detected in the exit stream of the reactor, but it was not quantified since its production was dictated by stoichiometry. The catalyst V(0.76)-3.8 displayed an enhancement of the consumption of oxygen that specifically promoted the production of CO_2 , **Figure 12**. In this sense, the recorded trends may be related to the difference in the nature of the oxygen belonging to the lattice of the active phase and the oxygen chemically adsorbed on the catalyst; these differences were already discussed in the XPS section of the paper. In addition, various authors have postulated that adsorbed electrophilic oxygen is responsible for the combustion of the alkanes in oxidation reactions.[8,10,13,138] Such an analysis also agreed with the studies of Chen et al.[139,140] who concluded that the rate of formation of propene is independent, zero order, of the partial pressure of oxygen for conventional oxide supported catalysts. In addition, the catalysts V(0.76)-3.8 and V(1.59)-9.0 produced measurable traces of H_2 and CH_4 at 500°C. Comparing the behavior of the catalysts synthesized at acidic pH with the one at basic pH, the former had larger yields to CO_2 than to C_3H_6 . Particularly, at 500°C, the yields to CO_2 over these catalysts were roughly up to fourfold larger than the yields to C_3H_6 . Meanwhile, the ratio between the yields to CO_2 and C_3H_6 was close to one. Finally, it was observed that the yields to C_3H_6 were always higher than the yields to CO for all the catalysts.

An analysis of the selectivity to C_3H_6 at 500°C is presented next. The catalysts V(1.30)-1.5 and V(0.76)-3.8 showed almost the same average steady state selectivity to C_3H_6 ; namely, 0.061 ± 0.016 and 0.068 ± 0.003 , respectively, despite the differences in the conversion found for these two catalysts. For the catalyst V(1.59)-9.0, the average steady state selectivity to C_3H_6 was 0.152 ± 0.003 ; a value which was the highest for all catalysts while the conversions of both O_2 and C_3H_8 were the highest, **Figure 12**. Also for V(1.59)-9.0, after ramping down the temperature to 450°C the steady state selectivity to C_3H_6 was slightly higher; 0.185 ± 0.001 , for conversions of C_3H_8 and O_2 of 0.058 and 0.044, respectively. These results thus ratified that the catalyst V(1.59)-9.0 performed best among all the sodium vanadate based catalysts. Additional analysis of the dependency of selectivity with the conversion of conversion, **Figure S17**, showed that within the range of conversion obtained for V(1.30)-1.5 and V(0.76)-3.8, **Figures S17a** and **S17b**, respectively, the selectivities to propene and CO_2 were negatively but weakly affected by conversion while the selectivity to CO was positively but weakly affected by conversion. Meanwhile, V(1.59)-9.0 showed the same kind of effects as above but with relatively higher intensity, **Figure S17c**. The above effects of conversion over selectivity for the sodium vanadate catalysts were, in general, similar in nature to those observed for the VO_x/SiO_2 benchmark, **Figure S17d**, and to those reported in the literature [8,10,13,22].

Concerning products yields for VO_x/SiO_2 , **Figure S15b**, CO_2 was the main reaction product followed but C_3H_6 , while CO was produced at significant amounts only at 500°C, where traces of H_2 were also detected. The observed products yields, the average steady selectivity to C_3H_6 changed with temperature as follows: at 350°C: $SC_3H_6 = 0.323\pm0.003$ ($XC_3H_8 = 0.022\pm0.000$, $XO_2 = 0.0002\pm0.0002$), at 400°C: $SC_3H_6 = 0.326\pm0.004$ ($XC_3H_8 =$

0.003 ± 0.001 , $XO_2 = 0.010 \pm 0.001$), at 450°C : $SC_3H_6 = 0.290 \pm 0.002$ ($XC_3H_8 = 0.049 \pm 0.001$, $XO_2 = 0.048 \pm 0.001$), and, at 500°C : $SC_3H_6 = 0.127 \pm 0.042$ ($XC_3H_8 = 0.126 \pm 0.003$, $XO_2 = 0.309 \pm 0.002$). Therefore, at 500°C , the selectivity to C_3H_6 displayed by the benchmark was lower than the selectivity displayed by the catalyst $V(1.59)-9.0$ ($SC_3H_6 = 0.152 \pm 0.003$) at the same level of conversion of propane, $XC_3H_8 = 0.100 \pm 0.001$, but with a lower consumption of oxygen, $XO_2 = 0.111 \pm 0.001$.

The results described above ratify that the catalyst $V(1.59)-9.0$ which is based on dispersed sodium vanadate particles of the α - NaVO_3 type phases constituted mainly by V^{4+} species and had lower basicity performed best. The recent literature has shown similar results in the case of both Na doped silica supports over which 2D vanadium oxide structures are formed [44,45] and sodium vanadates were impregnated over silica, see **Table S7** [46,84]. Particularly, Grant and co-workers [44,45] used both a silica where Na was present as an impurity (Na-SiO_2) and a silica over which a solution of NaNO_3 was impregnated as supports for vanadium oxides whose impregnation was made with a dry isopropanol solution of vanadium triisopropoxide under a dry N_2 atmosphere. For the catalysts synthesized over the Na-SiO_2 support, the authors reported the formation of V_2O_5 nanoparticles whose propane conversion was kept below 0.09, $T = 490^\circ\text{C}$, O_2/C_3H_8 molar ratio = 0.5 -so-called reducing conditions-, and whose selectivity decreased from $SC_3H_6 \sim 0.60$ at $XC_3H_8 \sim 0.02$ to $SC_3H_6 \sim 0.40$ at $XC_3H_8 \sim 0.07$ as a function of dispersion; namely, higher dispersion led to 2D vanadium oxide structure that were more active, i.e., higher apparent TOFs, and selective to propene than Na promoted V_2O_5 nanoparticles. On the other hand, Nadjafi et al.[46,84] impregnated aqueous solutions of NaVO_3 and sodium decavanadate, $\text{Na}_6V_{10}O_{28}$, mixed with oxalic acid over silica. The authors tested their catalysts at 450°C using the same O_2/C_3H_8 molar ratio as Grant et al.[44,45] The importance of the latter condition is not to be neglected since it is known that reducing conditions lead to higher propene selectivities.[141,142] In contrast, the current work used so-called oxidizing conditions; namely, the O_2/C_3H_8 molar ratio was 2.0, which has been established to lower selectivity to propene.

Let us now analyze the effects of the pH, the concentration of vanadium in solution during impregnation, and their interaction over the apparent turnover rates of C_3H_8 and O_2 at 500°C . **Figures 14** and **S18** show main effects and interaction plots, respectively, done for this purpose.

The reader may find discriminated turnovers for each tested catalyst in **Tables S8** and **S9**. Results of this analysis showed that only the pH had a statistically positive significant effect over the apparent turnovers of C_3H_8 and O_2 . This effect produced larger apparent turnovers for the catalysts synthesized at $\text{pH}=3.8$ and $\text{pH}=9.0$; where, the average C_3H_8 and O_2 apparent turnovers for these latter two types of catalysts were not statistically different. The input variables studied during synthesis did not have non-additive effects over the apparent turnovers as evidenced in **Figure S18**. From characterization results, the above trends seem rather related to the already described differences in vanadium dispersion, reducibility, and acid-base properties.

Figure 14. Main effects plots for assessing the effects of pH, vanadium concentration in solution over the apparent propane and oxygen turnover rates during the oxidation of propane. Reaction conditions: Propane GHSV = 4 h^{-1} , 500°C , feed composition = 5:10:115 [mL NTP /min] $C_3H_8:O_2:N_2$, p = atmospheric pressure (Bucaramanga ~ 0.89 bar).

On the other hand, the catalytic results led postulate to the following reaction paths for propane oxidation, **Scheme 1**. Accordingly, propene may be produced either by the direct dehydrogenation of propane (A) or via the indirect oxidative route (B). Regardless of the route, one may notice that the desorption constants, $K_{\text{des-A}}$ and $K_{\text{des-B}}$, play a key role in determining the selectivity of the catalyst. Roughly, these desorption constants must be large enough as to favor the desorption of propene rather than its further oxidation and combustion. Adsorption constants are a function of the enthalpies and entropies of adsorption of the surface intermediates. In this sense, while enthalpy is a measure of the strength of the interaction between the active phase (⚡) and the adsorbed intermediates, entropy is a measure of the degree of coordination of the adsorbed intermediates with the active phase. For the oxidative dehydrogenation of propane, this translates into the need of a catalyst with an oxidizing active phase able to break one of the C-H bonds of propane, form a surface allylic double bond, and then desorb propene before it can undergo further oxidation. At present, it is well accepted that the active sites for hydrocarbon oxidation over vanadium based catalysts are surface oxygen moieties linked to vanadium.[8,9,138,140,143–145,10,12,13,26–29,31] These moieties are consumed by the reaction and then replenished by oxygen from the gas phase that is activated by surface vanadium, hence completing a redox cycle. The turnover rate of the redox cycle can thus be considered to depend in part on the Lewis acidity of the vanadium moieties. Therefore, more acidic vanadium species would be able to do faster turnovers provided that a very fast rate of surface diffusion of the activated oxygen happens. However, given the consecutive pathway of propane oxidation, the faster the surface diffusion of activated oxygen in the catalyst is the higher the probability of burning the adsorbed hydrocarbon intermediates.

H_2 -TPR results showed that the reduction of the sodium vanadate based catalysts started at lower temperatures as compared to the VO_x/SiO_2 benchmark, **Figure 6**; a finding that has been reported

earlier.[9,32,42,46,146] Overall, sodium, and other alkalis, increase the reducibility of the vanadate moieties and, in turn, regulate, to some extent, the rate of oxygen transfer to the activated surface hydrocarbons. In this sense, Martín et al.[147] reported that sodium in vanadium oxide supported catalysts strongly weakens the adsorption of propene over vanadium oxide to an extent where it is reduced to physisorption and this thwarts the reduction of V^{5+} to V^{4+} . The presence of sodium would increase K_{des-B} in the oxidative dehydrogenation route of reaction.

Scheme 1. General reaction paths on the catalytic oxidation of propane.

Another aspect worth considering is how the strong consumption of oxygen by the catalyst seemed to directly translate into CO_2 production, **Figure 12**. In this regard, Oyama and others[138,148] established that the oxidative dehydrogenation of ethane to ethene and other selective oxidation products is structure insensitive while the oxidation of ethane to CO_x is structure sensitive. Taking advantage of the variations in the number of active sites found for the four replicates of the catalyst V(1.59)-9.0, **Table S4**, an analysis of the structure sensibility of the reaction in terms of both the turnover rates of propane and of oxygen is presented next.

Figure 15 plots the apparent steady state turnover rates of propane and oxygen as a function of the initial number of active sites of the four replicates of the catalyst as measured at 500°C. The four experimental averages presented in these plots are compared to a 95% t-Student confidence interval, $v = 32$, for the global average of all measurements. Given that all the experimental points fell out of the corresponding confidence intervals, the observed effects were statistically significant. Therefore, both the transformation of oxygen and of propane were structure insensitive. This was in agreement with previous literature studies [138]. **Figure 16** plots the apparent steady state TOFs for propene, CO_2 , CO, and H_2 as a function of the apparent TOF of the reactants. The slopes of the rates for propene and CO_2 were the same in each plot. This indicated that the reactions that led to both products had the same reaction rate constants; a fact that corroborates that both reactions are kinetically controlled by the same elementary step. Furthermore, the apparent TOFs for propene were within the range of those reported by other authors who have investigated the catalytic performance of either Na-promoted 2D VO_x/SiO_2 [44] or $Na_6V_{10}O_{28}/SiO_2$ and $\alpha-NaVO_3/SiO_2$ [46] in propane oxidation under reducing reaction atmospheres, see **Tables S7 – S9** for comparison purposes. Consequently, the current results confirm previous kinetic studies that demonstrated that the production rate of propene has a zero order dependency on oxygen concentration [139,149,150].

Figure 15. Apparent average steady state turnover rates as a function of the quantity of surface vanadium for the catalysts V(1.59)-9.0. Reaction conditions: Propane GHSV = 4 h⁻¹, feed composition = 5:10:115 [mL NTP /min] $C_3H_8:O_2:N_2$, $T = 500^\circ C$, p = atmospheric pressure (Bucaramanga ~ 0.89 bar). The plotted points correspond to averages from the steady state behavior during catalytic tests.

Figure 16. Apparent median steady state turnover rates for the reaction products as a function of the apparent median steady state turnover rates of propane and dioxygen for the catalysts based on sodium orthovanadate. Reaction conditions: Propane GHSV = 4 h⁻¹, feed composition = 5:10:115 [mL NTP /min] $C_3H_8:O_2:N_2$, $T = 450^\circ C$, p = atmospheric pressure (Bucaramanga ~ 0.89 bar). The plotted points correspond to samples from the four replicates of the synthesis of the same catalyst: V(2.66)-9.0.

According to the literature, the activation of one of the C-H bonds of propane is the rate determining step in the oxidation of propane.[8–10,12,35,138,139] Particularly, Chen et al.[139] showed that the oxidative dehydrogenation of propane and its combustion have similar activation energies hence the steps that determine the selectivity propene/ CO_2 is defined for what may occur after the activation of the C-H bond of propane; which in turn depends on the ratio K_{des-B}/k_3 , **Scheme 1**. Therefore, in this case, the highest production of propene for the catalysts synthesized at pH=9.0 may be ascribed to sodium decreasing the adsorption energy of propene, as discussed previously. On the other hand, the slopes of the straight lines for CO were always ca. half of the slopes for propene and CO_2 . Therefore, the rate constant for producing CO should be half the rate constant for propane activation. This suggested that CO production followed the same reaction path as CO_2 . Finally, the slopes for the linear relationships for the TOFs of hydrogen as a function of the TOFs of the reactants were very small and negative as compared to the other products hence suggesting that the detected H_2 could be formed by a reaction mechanism other than the one followed for oxidative dehydrogenation. Namely, hydrogen could have been produced either by direct dehydrogenation, route A, **Scheme 1**, or by the reforming of propane, e.g. **Equation (v)**. Aiming to get an insight into the production of H_2 , further analysis of the thermodynamics of the system ($p = 1$ atm; O_2/C_3H_8 molar ratio = 2) was carried out by means of the Chemical Equilibrium Calculation tool available for

free at: <http://navier.engr.colostate.edu/code/code-4/index.html>. According to the authors, this tool is based on the STAJAN interactive program developed by Reynolds using the element potential method for equilibrium analysis. **Figure 17** shows the dependency on temperature (a1) of the propane and oxygen conversion when H₂ is produced (**Figure 17a1**), the equilibrium molar fractions of C₃H₆, CO₂, CO, H₂O, and H₂ for case (a1) (**Figure 17a2**), (b1) the propane and oxygen conversion when no H₂ is produced (**Figure 17b1**), and (b2) the equilibrium molar fractions of C₃H₆, CO₂, CO, and H₂O for this case (**Figure 17b2**).

The results of the thermodynamic analysis show that under the current conditions, oxygen is always fully consumed. Meanwhile, propane reached full conversion at 500°C when hydrogen was produced (**Figure 17a1**), but the maximum conversion of propane was 0.70 at 700°C when hydrogen was not produced (**Figure 17b1**). On the other hand, when hydrogen was produced (**Figure 17a2**), its production started at ~150°C and then increased simultaneously with the decrease in the equilibrium molar fraction of water.

Figure 17. Thermodynamic equilibrium plots for the dependency on temperature (a1) of the propane and oxygen conversion when H₂ is produced (**Figure 17a1**), the equilibrium molar fractions of C₃H₆, CO₂, CO, H₂O, and H₂ for case (a1) (**Figure 17a2**), (b1) the propane and oxygen conversion when no H₂ is produced (**Figure 17b1**), and (b2) the equilibrium molar fractions of C₃H₆, CO₂, CO, and H₂O for this case ((**Figure 17b2**). Reaction conditions: standard pressure $p = 1.0$ bar; O₂/C₃H₈ molar ratio = 2. Plots made with the Chemical Equilibrium Calculation app available for free at: <http://navier.engr.colostate.edu/code/code-4/index.html>.

In addition, under the aforementioned conditions, the molar fraction of CO₂ remained approximately constant up to 400°C whence its production decreased until reaching a minimum at ~650°C. Conversely, the molar fraction of CO increased up to 0.35 at the latter temperature. Concerning propene, its maximum equilibrium molar fraction was reached between 450 – 475°C, but the estimated fractions were three orders of magnitude lower than

those estimated for the other reaction products. On the other hand, when no hydrogen was included in the system (**Figures 17b1** and **17b2**), the equilibrium molar fraction of propene increased one order of magnitude, while the molar fractions of CO₂ and CO showed the same trends as those previously described considering the formation of H₂ (**Figure 17a2**). In addition, the molar fraction of H₂O remained rather constant within the studied temperature range. The thermodynamic behavior discussed so far, allow establishing that the reactions described by the equations (i)-(v), Introduction section and **Figure S1**, do not suffice to describe the chemical equilibrium of the system. Particularly, the fact that the production of both H₂ and CO increased while H₂O and CO₂ were consumed suggest that at equilibrium conditions propane reforming with H₂O ($\text{C}_3\text{H}_8 + 3\text{H}_2\text{O} \rightleftharpoons 3\text{CO} + 7\text{H}_2$, $\Delta H_{25^\circ\text{C}}^0 \approx 499 \frac{\text{kJ}}{\text{mol}}$) and CO₂ ($\text{C}_3\text{H}_8 + 3\text{CO}_2 \rightleftharpoons 6\text{CO} + 4\text{H}_2$, $\Delta H_{25^\circ\text{C}}^0 \approx 622 \frac{\text{kJ}}{\text{mol}}$) [21,151] play an important role. Furthermore, according to thermodynamics, under the current reaction conditions -oxidizing environment-, the reforming reactions are more relevant for the production of H₂ than the endothermic direct dehydrogenation or propane ($\text{C}_3\text{H}_8 \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2$, $\Delta H_{25^\circ\text{C}}^0 \approx 128.10 \frac{\text{kJ}}{\text{mol}}$, $\Delta G_{25^\circ\text{C}}^0 \approx 87.69 \frac{\text{kJ}}{\text{mol}}$ [152]) and than the water gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$, $\Delta H_{25^\circ\text{C}}^0 \approx -41.17 \frac{\text{kJ}}{\text{mol}}$, $\Delta G_{25^\circ\text{C}}^0 \approx -28.53 \frac{\text{kJ}}{\text{mol}}$) which has been used for producing H₂ when the oxidation of propane is made over vanadium oxide based catalysts and under reducing conditions.[10,23,153]

Conclusions

The effects of pH, the concentration of vanadium in solution, and of their interaction; i.e., non-additive effect, over the properties of Na-SiO₂ (hollow vesicles, surface area ~18 m²/g, mesopores of average diameter of ~11 nm, and ~1.0 wt.% Na) supported catalysts used for the oxidation of propane under oxygen rich conditions, O₂/C₃H₈/ molar ratio = 2.0, were studied in this work. (1) Neither the pH and the solution concentration of vanadium did not influence the net difference between the nominal and final loadings of vanadium in the catalysts (~10%) nor their surface area and porosity. However, all catalysts presented a ~50% decrease in surface area due to partial mesopore blocking reflected by a ~30% increase in the average pore diameter. (2) The Na present in the support as either extra-framework (majority); i.e., ≡Si-O-Si-O-Na⁺, or intra-framework (minority); i.e., ≡Si-O-Na⁺ reacted with the dissolved NH₄VO₃ and led to the formation of different sodium metavanadates depending on the pH. Namely, when the pH was 1.5, i.e., below the point of zero charge of the support, PZC=3.5, large self-supported α-NaVO₃ (majority) and β-NaVO₃ (minority) microcrystals mixed with particles from the support were found in the hydrated catalysts. At pH=3.8 ~ PZC, both self-supported microcrystals β-NaVO₃ (majority) and α-NaVO₃ (minority) and clumps of sodium metavanadate particles were found in the hydrated catalysts. While, at pH=9.0 nanoparticles of sodium metavanadates were found most likely making a dispersed gel in the hydrated state of the catalysts. After dehydrating the catalysts, an interconversion between the α-NaVO₃ and β-NaVO₃ phases was evidenced. In general, the surface of the catalysts synthesized with low concentrations of vanadium in solution was enriched by

sodium. (3) The reducibility of the catalysts was a function of the impregnation pH, where the catalysts synthesized at pH=3.8 and 9.0 displayed similar reduction patterns but lower reducibility than the catalyst synthesized at pH=1.5. The produced patterns were correlated to the existence of a mixture of V^{5+} and V^{4+} species among which V^{4+} was prevalent for the catalysts synthesized at pH=3.8 and 9.0. As a consequence, the basicity of the catalysts decreased with the increase in pH. (5) The surface concentration of vanadium increased with the increase in the concentration of vanadium in solution, while the pH had a weak negative effect over the former. On the other hand, it was established that chemical surface state of oxygen in the synthesized catalysts was influenced weakly by the synthesis pH and, more importantly, by non-additive effects between the pH and the concentration of vanadium in solution. The latter was coherent with the detection of surface oxygen species related to the partial dissolution of the Na-SiO₂ support; a phenomenon that seemed to be favored at acidic pH. (6) It was established that, under the studied reaction conditions, the catalysts synthesized at pH=3.8 and pH=9.0 displayed an initial increase in the conversion of both reactants. Among the sodium vanadate based catalysts, those synthesized at pH=9.0 displayed the best performance in terms of the selectivity to propene and oxygen consumption. Furthermore, these catalysts displayed similar selectivity than a VO_x/SiO₂ benchmark whose oxygen consumption was higher. In this sense, the behavior of the catalysts synthesized at pH=3.8 allowed establishing that when the consumption of oxygen by the catalyst was higher than the conversion of propane, the reaction was more strongly directed towards a larger production of CO₂. An analysis of the apparent turnover rates recorded for the catalysts synthesized at pH=9.0 allowed establishing that both the catalytic reactions of propane and oxygen are structure insensitive. Furthermore, the collected evidence allowed corroborating that both the oxidative dehydrogenation of propane to propene and its combustion to CO and CO₂ are kinetically controlled by the initial activation of one of the C-H bonds of propane. The ensemble of these findings contributes to the understanding of sodium promoted vanadium oxide systems supported on silica; a topic that has been reinvigorated very recently. An analysis of the Raman spectra of the spent catalysts suggested that under the applied reaction conditions, all catalysts were provided of an active phase constituted by a mixture of α -NaVO₃ and β -NaVO₃ phases. Therefore, the observed differences in catalytic behavior were rather associated to changes in particle size, reducibility, and acidity.

Experimental section

Synthesis of catalysts. The sodium loaded, ca. 1.0 wt.%, silica -Na-SiO₂- support (commercial grade, Brazilian origin) was impregnated with NH₄VO₃ (Carlo Erba, pure reagent). Impregnation experiments were planned and executed by following a four times replicated 2² plus one off-centered point full factorial experimental design where the input variables were the pH and the concentration vanadium in the impregnation solution. The syntheses were made in random order as in agreement with the principles of statistical experimental design.[52–54] The levels selected for the pH were 1.5; 3.8; and 9.0, while for the molal (m) concentration of vanadium the levels were 0.0126×10⁻³; 0.0504×10⁻³; and 0.0864×10⁻³ molal. The values of pH were selected to be below, near, and above the point of zero charge, PZC, of the Na-SiO₂ support; PZC ~ 3.5, **Figure S1**. Synthesis runs were planned for producing batches of 3.0 g of the materials. Therefore, the nominal wt.% of vanadium in the catalysts were: 0.21, 0.84, and 1.44 wt.%. For each run, NH₄VO₃ was added to a beaker with 50 mL of deionized water (Milli-Q) at

70°C and stirred with a PTFE magnetic bar at 200 rpm to ensure the dissolution of NH₄VO₃. The pH of the resulting solution was adjusted with solutions of either HNO₃ (Merck, 65%) or NH₄OH (Merck, 25%). Afterwards, the necessary amount of the Na-SiO₂ support was added to the solution. The obtained suspension was heated to 90°C under 300 rpm stirring until evaporating most of the excess water. The formed slurry was further dried overnight at 100°C and then calcined at 500°C under 100 mL/min of dry air (Linde, dry grade) for 12 h. For reference purposes, bulk vanadium oxide was synthesized by calcining NH₄VO₃ at 120°C for 1 h and then at 550°C for 6 h. In addition, a SiO₂ supported vanadium oxide catalyst used as a benchmark was synthesized by the wetness impregnation of a solution of NH₄VO₃ in oxalic acid (NH₄VO₃/oxalic acid = 0.5 M). The concentration of vanadium in solution corresponded to 0.0864×10⁻³ molal; i.e., the high level of the experimental design. For the synthesis, Na was first removed from the original Na-SiO₂ material by first mixed in a beaker with a 1M HNO₃ solution for 4 h at 70°C and under 100 rpm magnetic stirring. The resulting suspension was vacuum-filtered and washed with deionized water until the washing solution had pH=7. The slurry recovered by filtration was dried for 24 h at 120°C and then calcined at 450°C in a static oven for 4 h. The removal of Na from the SiO₂ support was verified by collecting high resolution X-ray photoelectron spectroscopy spectra for the Na 1s region before and after the procedure, see **Figure S2**. The sodium free SiO₂ support was then added to the NH₄VO₃/oxalic acid solution under continuous stirring at 70°C. The resulting material was thermally treated in the same manner as the sodium loaded catalysts.

Assessment of physicochemical properties

Point of zero charge of the Na-SiO₂ support. The point of zero charge of the Na-SiO₂ support was determined by a potentiometric titration procedure. For the procedure, ca. 1.0000 g of Na-SiO₂ were suspended in 50 mL with a 0.05% solution of NaNO₃. The suspension was equilibrated under such conditions. Afterwards, doses of 0.05 mL of NaOH were automatically added to the suspension in the presence of NaCl as electrolyte. The change in pH was recorded as a function of the added volume of NaOH. The experiments were made with a Metrohm AG instrument controlled by the TIAMO® software. From the results of this test, the surface ionization constants (pK_a) were calculated and the corresponding acid-base distribution function for the solid was built, **Figure S1**.

Bulk vanadium content. The bulk contents of vanadium of the catalysts were measured by atomic absorption. Samples were dried for 2 h at 110°C in a 100 mL/min flow of air (Linde, dry grade) before the analyses. The digestion of the samples was done following the protocol proposed by Westerman et al.[154] For this purpose, ca. 0.5000 g of the samples were transferred to a polytetrafluoroethylene beaker where they were put in contact with a mixture between 2 to 5 mL of sulfuric acid (Merck, 95-97%) and 5 mL of hydrofluoric acid (Merck, 40%) under heating at 80°C. The procedure was stopped when sulfur trioxide fumes appeared since this indicates that silica has been completely dissolved and that the excess hydrofluoric acid has been evaporated. The cooled digests were diluted to 100 mL with deionized water and stored in polythene jars for performing the atomic absorption test. The nomenclature adopted for the synthesized materials was made by considering the results of the atomic absorption analyses. Thus, the catalysts were branded as V(y)-z. Where, y is the wt.% of vanadium of the materials as measured by atomic absorption, and z is the pH used for the synthesis.

Morphology, porosity, and surface area. The morphology of the materials was assessed by taking images with a scanning electron microscope, SEM. SEM measurements were made in a FEI Quanta 650 FEG instrument operated at an acceleration voltage of 15.00 kV. The analyzed samples were placed on top of carbon adhesive tape and coated with gold for alleviating differential charging effects during the tests. In addition, energy dispersive spectroscopy, EDS, were made over some particles of the materials analyzed by SEM with an EDAX APOLO X detector whose resolution was 126.1 eV (Mn K α line). EDS tests allowed estimating the chemical composition of some specific particles from selected materials.

The porosity of the materials was assessed after measuring the adsorption-desorption isotherms of molecular nitrogen at -196°C. For these measurements, samples of ca. 0.1500 g of each material were weighed inside 9 mm diameter cells made of borosilicate glass (Micromeritics). After weighing, the cells were placed in an outgassing unit (Vac Por 061, Micromeritics) and heated for 2 h at 200°C in order to remove adsorbed gases. The duration of the outgassing procedure was defined after finding that the vacuum in the cells reached ca. 0.05 mbar. The weight of the outgassed samples was recorded and used as input data for recording the adsorption-desorption isotherms. The adsorption-desorption isotherms for

each sample were measured in a 3FLEX™ (Micromeritics) instrument. Data were recorded in the relative pressure range (P/P_0) between 0.0025 and ~0.9900 using an equilibration time of 10 s. The total pore volume and the pore size distributions were calculated with the Barret-Joyner-Halenda, BJH, method[155] using the MicroActive® software provided with the instrument. However, the produced distribution can only be considered for comparison purposes since the software is restricted to pores with cylindrical geometry. In addition, the total specific surface area - SSA_{BET} - of the solids was estimated by the Brunauer-Emmett-Teller, BET, method.[156] The selection of the experimental points used for SSA_{BET} calculations was made after applying the Rouquerol transform[157] and checking for the so-called consistency criteria. On the other hand, to analyze whether nanoparticles of sodium vanadates formed inside the pores of the support, normalized SSA_{BET} , N_{SSABET} , values were calculated using the following equation (S1):[63]

$$(S1) N_{SSABET} = \frac{SSA_{BET}^{catalyst}}{SSA_{BET}^{Na-SiO_2}} \times (100 - y)$$

Where, $SSA_{BET}^{catalyst}$ = BET specific surface area of the catalysts and y = weight fraction of vanadium. The interpretation of equation (vi) considers that N_{SSABET} values near 1.0 correspond to very well dispersed supported phases that do not form nanoparticles causing pore blocking.[63,158]

Chemical structure. Raman, UV-vis diffuse reflectance spectroscopic, and X-ray diffraction measurements were done for characterizing the chemical structure of the catalysts. Raman analyses were done for hydrated and dehydrated samples of the fresh and spent catalysts. The dehydration procedure was made under vacuum in the same outgassing unit used for the adsorption experiments. The procedure consisted of drying samples of ca. 0.0500 g at 120°C for 1 h, and then overnight at 300°C. Right after completing the aforementioned treatment, the dehydrated samples were put in sealed bags containing a silica gel desiccant and then rapidly taken out of the bags, deposited over a quartz film of 1 mm of thickness, and transferred to the previously set-up Raman instrument. Spectra were recorded making 40 scans within the range 30 to 1700 cm^{-1} , step of 1.85 cm^{-1} , with a LabRAM HR Evolution Raman Confocal Spectrometer (HORIBA Scientific). The power of the laser of the instrument was fixed at 80 mW. The total acquisition time for recording the spectra depended on the intensity of scattered radiation and ranged from 10 to 500s. The resolution of the instrument was 1 cm^{-1} , the size of the aperture hole 50 μm , and the grating size 600 grooves/mm. Under these conditions, no degradation of the analyzed samples was observed.

For the UV-vis diffuse reflectance, UV-vis-DRS, measurements, the hydrated samples were ground in an agate mortar together with a BaSO₄ matrix. A film of the finely ground powder was deposited on a small quartz plate which was further covered with another quartz plate of equal size. The UV-vis-DRS spectra were recorded with a UV 2401PC spectrometer (Shimadzu) within the range 190-900 nm using a step of 1 nm and 70 scans. Data treatment was made after applying the Kubelka-Munk function $F(R_{\infty})$ which depends on the absorption energy $h\nu$, using the equation (S2):[159]

$$(S2) F(R_{\infty}) = \frac{(1-R_{\infty})^2}{2R_{\infty}}$$

Where, R_{∞} represents the diffuse reflectance measured from a semi-infinite layer.

Edge energies, E_g , were determined from plots of $(f(R) \cdot h\nu)^2$ as a function of absorption energies and then applying the Tauc method[160] and following the recommendations by Makula et al.[161] On the other hand, fitting of the recorded spectra was done using the method recommended by Bulanek et al.[91,162] and with the help of the Fityk program (available for free at: <https://fityk.nieto.pl/>).

Finally, X-ray diffraction (XRD) measurements were performed in a BrukerD8 Advanced - Davinci diffractometer equipped with a Cu-K α radiation source and a Lineal LynxEye detector. Diffraction patterns were recorded between $2\theta = 2.0$ and 70° , with a step time of 0.6 s which corresponds to a 2θ step of 0.02035°.

Reduction profiles of the catalysts. The reduction profiles of the catalysts were recorded using H₂ temperature programmed experiments, TPR. Tests were done in a CATLAB system coupled to a QGA mass spectrometer -MS- (Hidden Analytical). The MS was equipped with both an internal dual electron

multiplier detector, SEM, and a Faraday detector, and with a precision quartz inlet heated capillary (QIC) sampling interface. Samples of ca. 0.1000 g were loaded in a quartz tube (1.0 cm i.d.) and pretreated with a 50 mL/min flow of argon at 120°C for 1 h and then at 300°C for 2 h. After cooling down to 50°C, the reactor was fed with a mixture of 2 vol% H₂ in Ar (50 mL/min) while the temperature was increased at 5°C/min and up to 900°C. The consumption of hydrogen and the production of water were followed on-line with the MS. The sensitivity factors provided by the Hidden QMS library were used for quantification. The instrument was calibrated with H₂ pulses of 10 μL for quantification purposes. However, due to the very low intensity of the acquired signals, it was necessary to approximate hydrogen consumption by calculating the peak area from the water signal. The following stoichiometry was assumed: one mole of H₂ per one mole of H₂O for every reduction step. Such an assumption was based on the following equation postulated for the removal of lattice oxygen from V₂O₅: [163]

Basicity of the catalysts. The basicity of the catalysts was analyzed by making CO₂ temperature programmed desorption tests. The tests were done in the same equipment as the one used for TPR. Samples of ca. 0.1000 g were pretreated with a 20 mL/min flow of argon at 120°C for 1 h and then at 300°C for 2 h. After cooling down to 50°C, the reactor was fed with a 20 mL/min flow of 10% CO₂ in Ar for 1 h. Then, the system was purged with Ar (30 mL/min) for 30 min before starting the test by raising the temperature to 600°C at 5°C/min, adapting the procedure described by Zhao et al.[164]

Surface chemistry. The near surface elemental composition and chemical speciation of the materials were assessed by X-ray photoelectron spectroscopy, XPS. XPS spectra were recorded in the XPS/ISS/UPS-A.Centeno surface characterization platform (SPECS). The platform is equipped with a PHOIBOS 150 2D-DLD analyzer and a monochromatic Al K α X-ray source (FOCUS 500). The X-ray source was operated at 100 W and 12 kV. For the analyses, the samples were deposited on a carbon conductive tape which was mounted on a metallic sample holder. Samples were placed inside the instrument via its introduction chamber for outgassing and then moved to the analysis chamber which was at a base pressure of ca. 1×10^{-7} Pa. Spectra were recorded after setting the pass energy of the analyzer at 100 eV, energy step equal to 1.000 eV, for recording general surveys and at 15 eV, energy step equal to 0.050 eV, for recording high-resolution spectra of specific core lines. The charge developed by the surface of the samples by the photoelectron emission process was compensated with an electron flood gun (FG 15/40-PS FG500) operated either between 1-10 eV or between 58-70 μA , as required for avoiding artificial chemical shifts and deformation of the recorded peaks. The stability of the samples during the analyses was verified by taking spectra from the C 1s core level at the beginning and at the end of each run. The data recorded for each sample were treated with the CasaXPS software (Casa Software Ltd.) using a U SiO₂ Tougaard[165] type baseline and with either LA(y_1, y_2) or TLA(y_1, y_2, y_3) line shapes. Scofield response sensitivity factors were used for quantification.[166]

Six random samples of the Na-SiO₂ support were analyzed. The objectives were: (1) to estimate the media of the empirical formula for the surface of the support and (2) to choose the most adequate core line for calibrating the binding energy scale of the spectra. On the other hand, twenty samples were analyzed from randomly selected replicates of the catalysts V(0.19)-1.5, V(1.30)-1.5, V(0.76)-3.8, V(0.19)-9.0, and V(1.59)-9.0.

The surface oxygen uptake capacity of the twenty synthesized materials was assessed by oxygen chemisorption. The measurements were made with a ChermiSorb 2720 (Micromeritics) instrument provided with a thermal conductivity detector (TCD). Prior to measurements, samples of weights between 0.8000 and 1.0000 g were placed inside a U-shaped quartz reactor and then outgassed under vacuum at 120°C for 1 h and further at 300°C for 2 h in the Vac Prep 061 unit mentioned earlier. Then, the samples were placed in the instrument where they were reduced under a flow of 40 mL/min of hydrogen (Linde, 99.99%) at 367°C during 2 h. At this temperature, pulses of 0.5 mL of oxygen (Cryogas, UHP) were injected to the testing port of the instrument using a calibrated syringe. Time intervals of 5 min were fixed between each injection. Injections were stopped after reaching the saturation of the sample which was evidenced from a stabilization of the value displayed for the area of the integrated signal from the TCD. TCD areas were transformed into oxygen concentrations [cm^3 of adsorbed oxygen/g sample] following equation (S3).

$$(S4) V_{ads} = \frac{V_{inj}}{w} \times \sum_{i=1}^n \left(1 - \frac{A_i}{A_f} \right)$$

Where, V_{inj} = volume of gas injected [cm^3]; w = sample weight [g]; A_i = area of peak i ; A_f = area of last peak; V_{ads} = adsorbed volume [cm^3/g].

The methodology adopted for the measurements was adapted from the method developed by Oyama et al.[36] According to these authors,[36] under the above mentioned conditions, a complete reduction of the surface of vanadium pentoxide, V_2O_5 , is achieved without reducing the bulk of the oxide. Herein, it will be assumed that these considerations may be extended to vanadium oxides other than V_2O_5 . For calculating the number of exposed vanadium sites, a stoichiometry of one mol of atomic oxygen per mol of exposed vanadium was assumed following the proposal by Nag et al.[167] Though the exactness of the method may be called into questioning, its results are nonetheless useful for comparison purposes. On the other hand, it will be assumed that the number of exposed vanadium sites measured with the current method is an acceptable estimation of the number of active sites, albeit the latter may correspond to oxygen moieties; namely, oxygen in V-O-V or V=O linkages, whose intrinsic reactivity in oxidation reactions varies.[9,26,31,32,79]

Catalytic tests

The catalysts were tested in the oxidation of propane. Tests were carried out in a fixed-bed stainless steel reactor with an internal diameter of 1.18 cm and provided with a porous plate of 10 μm of diameter that was used to support the catalytic bed. Reaction tests were done ramping the temperature from 350 to 500°C and then back to 350°C using steps of 50°C. A constant gas hourly space velocity of 4 h^{-1} referred to propane was used. Catalysts, ca., 0.3000 g of particles with sizes between 180 – 300 μm , were pretreated in-situ with a 130 mL/min of N_2 at 120°C for 1 h, followed by cooling to ambient temperature before feeding the reactor with the reactants. The reaction feed was composed of a 5:10:115 [mL NTP -NIST definition-/min] mixture of C_3H_8 : O_2 : N_2 set with mass flow controllers (Alicat). All tests were made at atmospheric pressure (~0.99 atm in Piedecuesta, Colombia). For the VO_x/SiO_2 benchmark, the reaction protocol was modified by doing the initial temperature ramping up stage up to 550°C and then the temperature was decreased 50°C stepwise to 350°C.

The reaction feed was analyzed at ambient temperature before and after the catalytic test. Reaction products were analyzed using an on-line gas chromatograph -GC- (Shimadzu GC-2014ATT) equipped with both thermal conductivity and flame ionized detectors. The system also has a methanizer for improving the accuracy of the quantification of CO and CO_2 . For the analyses, the reaction products were separated with both a HayeSep Q and a Molecular Sieve 5A column. Ar (20 mL/min) was used as carrier gas for GC analyses. The temperatures of the GC oven, the TCD, the methanizer, and FID were kept constant at 100°C, 160°C, 375°C, and 200°C, respectively. dry air, H_2 and Ar (carrier gas) were fed to the system at 35 kPa, 65 kPa, and 60 kPa, respectively. The quantification of the reaction products was made following the methods presented elsewhere.[168] The catalytic performance of the materials was analyzed using conversions - X_i - (equation S5), yields - Y_p -(equation S6), selectivity - S_p - (equation S7) using the methods described by Sandoval et al.[168], and apparent reaction rates considering a differential reactor. Further estimation of apparent turnover frequencies, TOF, [s^{-1}] were done with equation (S8), considering the concentration of surface vanadium of each type of catalyst as estimated from O_2 chemisorption experiments.

$$(S5) X_i = \frac{A_i^0 - A_i \cdot w}{A_i^0}; w = \frac{A_0}{A_s}$$

$$(S6) Y_p = \frac{n_p}{n_{\text{C}_3\text{H}_8}^0}$$

$$(S7) S_p = \frac{n_p}{n_{\text{CO}_2} + n_{\text{CO}} + n_{\text{C}_3\text{H}_6} + n_{\text{H}_2} + n_{\text{CH}_4}}$$

$$(S8) \text{Apparent TOF} = \frac{(\text{Molar flow of C}_3\text{H}_8) \cdot X_{\text{C}_3\text{H}_8}}{\text{mol of exposed V estimated by O}_2 \text{ chemisorption}}$$

Where, X_i refers to the conversion of either C_3H_8 or O_2 , A_i^0 is the initial area of the reactant, A_0 is the area of the reactant at a given time, w is the ratio between the initial and final areas (A_s) of the N_2 standard as estimated from the chromatogram, and n_p is the number of moles of a given product

Author Contributions

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Supplementary Information

1. Results

Table S1. Fulfillment of consistency criteria proposed by Rouquerol for the estimation of the specific surface area by the BET method. n_{mon} = monolayer capacity in moles.

Sample	$C_{\text{BET}} > 0$	$n(\text{min}) < n_{\text{mon}} < n(\text{max})$	$P/P_0(\text{mono}) \sim 1/(\sqrt{C} + 1)$	Linear	RSQ
Na-SiO ₂	142.8	True	True	True	0.99991
V(1.59)-9.0	242.3	True	True	True	0.99993
V(1.30)-1.5	207.3	True	True	True	0.99991
V(0.19)-1.5	235.3	True	True	True	0.99994
V(0.76)-3.8	197.4	True	True	True	0.99999
V(0.19)-9.0	202.9	True	True	True	0.99998

Table S2. XPS quantification for six samples of the Na-SiO₂ support as derived from high resolution spectra for each element.

Sample	Element mol %				
	Carbon	Sodium	Oxygen	Silicon	O/Si
SiO ₂ -1	1.58	1.42	62.65	34.35	1.82
SiO ₂ -2	1.82	1.52	61.27	35.39	1.73
SiO ₂ -3	3.32	1.37	60.93	34.38	1.77
SiO ₂ -4	2.47	1.34	61.46	34.73	1.77
SiO ₂ -5	2.22	1.40	61.28	35.10	1.75
SiO ₂ -6	2.78	1.40	60.78	35.04	1.73
Average	2.37	1.41	61.40	34.83	1.76
Standard error	0.26	0.03	0.27	0.17	0.01
$t_{\alpha=0.05, v=5}$	2.57				
Tails	0.67	0.06	0.70	0.44	0.04

Table S3. Estimated elemental compositions of the surface of samples of the V(x)-y catalysts by X-ray photoelectron spectroscopy. N.F. = Not found. BM = Benchmark.

Sample	Element mol %					
	Carbon	Sodium	Oxygen	Silicon	Vanadium	Nitrogen
V(0.19)-1.5-1	1.65	1.59	62.62	33.72	0.45	N.F.
V(0.19)-1.5-2	1.59	1.86	61.33	34.73	0.49	N.F.
V(0.19)-1.5-3	3.89	1.90	60.89	31.61	1.71	N.F.
V(0.19)-1.5-4	4.18	2.21	61.11	31.67	0.48	N.F.
V(0.19)-1.5-5	4.71	1.70	59.28	33.86	0.44	N.F.
V(1.30)-1.5-1	2.63	0.63	61.28	32.39	2.01	1.05
V(1.30)-1.5-2	4.08	0.82	61.61	29.63	3.11	0.76
V(1.30)-1.5-3	5.21	1.26	59.36	30.74	3.44	N.F.
V(1.30)-1.5-4	6.35	1.24	58.84	31.20	2.36	N.F..
V(0.76)-3.8-1	1.82	1.50	60.38	35.44	0.87	N.F.
V(0.76)-3.8-2	2.30	1.82	61.66	33.17	0.74	0.31
V(0.76)-3.8-3	3.45	2.02	61.25	32.58	0.70	N.F.
V(0.19)-9.0-1	1.65	1.56	62.62	33.72	0.45	N.F.
V(0.19)-9.0-2	1.59	1.86	61.33	34.73	0.49	N.F.
V(0.19)-9.0-3	1.50	2.04	61.35	34.89	0.22	N.F.
V(1.59)-9.0-1	2.76	1.59	60.01	34.06	1.58	N.F.
V(1.59)-9.0-2	2.15	1.44	60.54	34.77	1.09	N.F.
V(1.59)-9.0-3	8.92	1.72	56.22	31.41	1.73	N.F.
V(1.59)-9.0-4	4.05	2.09	60.01	32.23	1.62	N.F.
V(1.59)-9.0-5	3.96	1.67	59.97	32.84	1.55	N.F.
VO _x /SiO ₂ -BM	21.38	N.F.	53.76	21.61	3.25	N.F.

Table S4. Concentration of exposed vanadium sites as measured by oxygen chemisorption for one sample of each synthesis replicate of each type of catalyst.

Catalyst	Number of exposed vanadium sites (μmol)					
	Catalyst replicates				Average	Standard Error
	First	Second	Third	Fourth		
V(0.19)-1.5	11.9	9.5	16.2	13.5	12.8	1.4
V(1.30)-1.5	85.4	32.5	37.6	58.9	53.6	12.0
V(0.76)-3.8	17.7	12.4	14.9	16.2	15.3	1.1
V(0.19)-9.0	2.7	3.6	2.5	4.6	3.4	0.5
V(1.59)-9.0	14.7	24.1	41.5	39.3	29.9	6.4

Table S5. Quantification of the O 1s components considered for the O 1s core line of the studied materials. In some instances, the position of the O 1s – I component was constrained by employing a Δ parameter = position of the V 2p_{3/2} peak + 13.26 eV in line with literature proposals.^{34,35}

Sample	O 1s, Region		O 1s, components*						O 1s-I mol%	O 1s -I/V ratio
			O 1s -I		O 1s -II		O 1s -III			
	BE	FWHM	BE	FWHM	BE	FWHM	BE	FWHM		
Na-SiO ₂ -1	533.66	2.07	531.40	1.94	533.07	1.94				
Na-SiO ₂ -2	533.56	2.04								
Na-SiO ₂ -3	532.43	3.33								
Na-SiO ₂ -4	533.68	2.27								
Na-SiO ₂ -5	533.51	1.97								
Na-SiO ₂ -6	533.73	2.08								
V(0.19)-1.5-1	533.41	1.75	530.70	2.11	533.24	1.69	534.83	1.69	3.58	2.10
V(0.19)-1.5-2	533.28	1.86								
V(0.19)-1.5-3	533.63	2.12								
V(0.19)-1.5-4	534.30	2.47								
V(0.19)-1.5-5	533.52	1.92								
V(1.30)-1.5-1	533.33	1.82	530.55	1.65	533.28	1.65	534.53	1.65	2.05	1.02
V(1.30)-1.5-2	533.29	2.04	530.59	1.76	533.18	1.76	534.25	1.76	5.19	1.67
V(1.30)-1.5-3	533.51	2.69	530.47	2.02	532.12	2.02	533.65	2.02	3.42	0.99
V(1.30)-1.5-4	533.60	1.96	531.26	1.97	533.73	1.97			4.73	2.00
V(0.76)-3.8-1	533.06	2.55			533.12	1.87	535.06	1.87		
V(0.76)-3.8-2	533.58	1.97								
V(0.76)-3.8-3	533.67	2.15								
V(0.19)-9.0-1	533.30	2.03			532.55	1.91	534.01	1.91		
V(0.19)-9.0-2	532.97	2.90								
V(0.19)-9.0-3	533.28	2.02								
V(1.59)-9.0-1	533.14	1.85	530.72	1.80	533.08	1.80			3.36	2.13

V(1.59)-9.0-2	533.20	1.84	531.20	1.76	533.06	1.76				
V(1.59)-9.0-3	533.28	2.71							3.63	3.33
V(1.59)-9.0-4	533.79	2.53	531.16	2.46	533.87	2.46			1.36	0.84
V(1.59)-9.0-5	533.76	2.13	531.33	2.10	533.78	2.10			2.62	1.68

Table S6. Statistical assessment of the stability of the catalysts by comparing performances at 450°C before (↑) and after (↓) ramping up the temperature of the reactor to 500°C. Reaction conditions: propane GHSV = 4 h⁻¹, feed composition = 5:10:115 [mL NTP /min] C₃H₈:O₂:N₂, *p* = atmospheric pressure (Bucaramanga ~ 0.89 bar). The nomenclature of the materials is V(x)-y. Where, x = is the nominal mol.% of vanadium of the materials and y is the pH used for the synthesis. Aver = average, VarS = sample variance, Sp = pooled standard deviation considering equal population variances, t = experimental t-Student value.

Catalyst: V(1.30)-1.5				
	450°C↑		450°C↓	
	XC ₃ H ₈	XO ₂	XC ₃ H ₈	XO ₂
	0.008	0.004	0.010	0.006
	0.002	0.005	0.010	0.004
	0.004	0.004	0.007	0.007
	0.015	0.003	0.006	0.006
	0.033	0.023	0.025	0.014
	0.033	0.024	0.024	0.015
	0.032	0.023	0.024	0.015
	Aver	0.0181	0.0124	0.0150
VarS	2.00E-04	1.11E-04	7.82E-05	2.44E-05
t-test				
ΔAver	0.0031	0.0031		
Sp	0.0118	0.0082		
t	0.49	0.70		
p-value	0.63	0.50		
Catalyst: V(0.76)-3.8				
	450↑		450↓	
	XC ₃ H ₈	XO ₂	XC ₃ H ₈	XO ₂
	0.013	0.014	0.011	0.010
	0.008	0.014	0.007	0.011
	0.008	0.013	0.011	0.011
	0.012	0.011	0.008	0.009
	0.012	0.010	0.003	0.008
	0.013	0.010	0.002	0.009
	Aver	0.0111	0.0119	0.0070
VarS	5.17E-06	3.73E-06	1.36E-05	1.49E-06
t-test				
ΔAver	-0.0041	-0.0023		
Sp	0.0031	0.0016		

t	2.32	2.47		
p-value	0.04	0.03		
Catalyst: V(1.59)-9.0				
	450°C↑		450°C↓	
	XC ₃ H ₈	XO ₂	XC ₃ H ₈	XO ₂
	0.020	0.006	0.059	0.046
	0.021	0.006	0.057	0.044
	0.025	0.004	0.058	0.043
	0.010	0.006	0.060	0.042
	0.012	0.006	0.050	0.040
	0.009	0.009	0.049	0.040
	0.010	0.008	0.047	0.039
	0.010	0.010	0.046	0.036
	0.005	0.002	0.035	0.035
	0.005	0.002	0.041	0.036
	0.004	0.001	0.041	0.036
			0.038	0.035
			0.038	0.035
			0.027	0.025
			0.027	0.023
			0.025	0.022
Aver	0.0119	0.0056	0.0435	0.0360
VarS	4.74E-05	8.51E-06	1.34E-04	5.10E-05
t-test				
ΔAver	0.0316	0.0305		
Sp	0.0100	0.0058		
t	8.11	13.36		
p-value	1.83E-08	7.01E-13		

Table S7. Comparison of apparent reaction rates (TOFs) for the production of propene between literature reports and current work.

				Reaction conditions			
Authors	$X_{C_3H_8}$ (%)	r [mmol C_3H_8 / (mol Vxs)]	r [mmol C_3H_6 / (mol Vxs)]	O_2/C_3H_8 ratio	T [°C]	GHSV [h^{-1}]	Catalytic phase**
Grant et al.*	~1.5-8.5	5.3	5.3	0.5	490		Na-promoted VO_x
Nadjafi et al.*	~1.5-9.0	Not reported	~3.0 - 6.5	0.5	450	6.8	$Na_6V_{10}O_{28}$
			~1.2 - 4.3				α - $NaVO_3$
This work**	~2.6-5.8	~0.9 – 9.1	~0.6 – 1.3	2.0	450	4.0	α - $NaVO_3$ type phases
	~1.0-16.0	~1.5 – 23.3	~0.1 - 6.1	2.0	500	4.0	

*rates calculated from the bulk vanadium loadings assuming that vanadium is dispersed as 2D species.

**rates calculated from the concentration of surface vanadium as estimated from O_2 chemisorption experiments.

***All catalysts supported on SiO_2 from different origins.

For the table, it is worth mentioning that the rates reported by the above authors assumed that vanadium is dispersed over the support forming 2D structures hence the “mol V” term in the rates was estimated directly from the bulk content of the catalysts. Therefore, the authors implicitly assumed that all vanadium is exposed at the surface of the catalyst. In the case of our work, both bulk sodium metavanadate and nanoparticles were present in the catalysts. Therefore, “mol V” was estimated from O_2 chemisorption experiments.

Table S8. Average conversions, yields, and apparent turnover rates (TOF) for reactants and products during the oxidation of propane over V(x)-y catalysts. Calculations were made assuming a differential reactor and that the active sites correspond to the concentration of exposed vanadium [μmol] as measured by oxygen chemisorption. Reaction conditions: $T = 450^\circ\text{C}$, propane GHSV = 4 h^{-1} , feed composition = 5:10:115 [mL NTP /min] $\text{C}_3\text{H}_8:\text{O}_2:\text{N}_2$, p = atmospheric pressure (Bucaramanga ~ 0.89 bar). R# = replicate number of the synthesized catalyst. Nomenclature: x=vanadium oxide loading as measured by atomic absorption; y=pH. Na-SiO₂ was used as support.

T = 450°C						
Catalyst	X _{C₃H₈}	X _{O₂}	Y _{CO₂}	Y _{CO}	Y _{C₃H₆}	10 ³ ×Y _{H₂}
V(0.19)-1.5-R4	0.007	0.005	0.001	0.000	0.000	0.000
V(1.30)-1.5-R1	0.024	0.015	0.002	0.000	0.000	0.000
V(1.30)-1.5-R2	0.008	0.005	0.001	0.000	0.000	0.000
V(0.76)-3.8-R1	0.004	0.008	0.003	0.000	0.000	0.000
V(0.76)-3.8-R2	0.010	0.011	0.003	0.000	0.000	0.000
V(0.19)-9.0-R4	0.012	0.008	0.003	0.000	0.000	0.000
V(1.59)-9.0-R1	0.026	0.024	0.007	0.003	0.006	0.000
V(1.59)-9.0-R2	0.039	0.035	0.009	0.003	0.006	0.000
V(1.59)-9.0-R3	0.048	0.039	0.008	0.003	0.007	0.000
V(1.59)-9.0-R4	0.058	0.044	0.011	0.005	0.011	0.170
Apparent TOFs [s ⁻¹]						
Catalyst	TOF _{C₃H₈}	TOF _{O₂}	TOF _{C₃H₆}	TOF _{H₂}	TOF _{CO₂}	TOF _{CO}
V(0.19)-1.5-R4	1.73E-03	2.74E-03	0.000	0.000	6.38E-04	1.20E-04
V(1.30)-1.5-R1	9.86E-04	1.18E-03	0.000	0.000	1.98E-04	2.75E-05
V(1.30)-1.5-R2	8.50E-04	1.16E-03	0.000	0.000	2.94E-04	8.45E-05
V(0.76)-3.8-R1	8.56E-04	3.31E-03	0.000	0.000	1.32E-03	1.47E-04
V(0.76)-3.8-R2	2.67E-03	5.95E-03	0.000	0.000	1.55E-03	1.75E-04
V(0.19)-9.0-R4	9.12E-03	1.23E-02	0.000	0.000	3.82E-03	2.84E-04
V(1.59)-9.0-R1	6.21E-03	1.11E-02	1.32E-03	0.000	3.25E-03	1.32E-03
V(1.59)-9.0-R2	5.55E-03	1.01E-02	8.17E-04	0.000	2.55E-03	7.59E-04
V(1.59)-9.0-R3	4.21E-03	6.80E-03	6.19E-04	0.000	1.33E-03	5.63E-04
V(1.59)-9.0-R4	6.76E-03	1.02E-02	1.29E-03	1.97E-08	2.63E-03	1.13E-03

Table S9. Average conversions, yields, and apparent turnover rates (TOF) for reactants and products during the oxidation of propane over V(x)-y catalysts. Calculations were made assuming a differential reactor and that the active sites correspond to the concentration of exposed vanadium [μmol] as measured by oxygen chemisorption. Reaction conditions: $T = 500^\circ\text{C}$, propane GHSV = 4 h^{-1} , feed composition = 5:10:115 [mL NTP /min] $\text{C}_3\text{H}_8:\text{O}_2:\text{N}_2$, p = atmospheric pressure (Bucaramanga $\sim 0.89 \text{ bar}$). R# = replicate number of the synthesized catalyst. Nomenclature: x=vanadium oxide loading as measured by atomic absorption; y=pH. Na-SiO₂ was used as support.

T = 500°C						
Catalyst	X _{C₃H₈}	X _{O₂}	Y _{CO₂}	Y _{CO}	Y _{C₃H₆}	10 ³ ×Y _{H₂}
V(0.19)-1.5-R4	0.017	0.018	0.006	0.001	0.002	0.152
V(1.30)-1.5-R1	0.037	0.020	0.006	0.001	0.003	0.000
V(1.30)-1.5-R2	0.033	0.042	0.013	0.003	0.004	0.820
V(0.76)-3.8-R1	0.049	0.083	0.029	0.004	0.007	1.100
V(0.76)-3.8-R2	0.061	0.098	0.033	0.005	0.008	1.790
V(0.19)-9.0-R4	0.020	0.027	0.010	0.001	0.002	0.000
V(1.59)-9.0-R1	0.099	0.110	0.029	0.014	0.026	1.200
V(1.59)-9.0-R2	0.097	0.110	0.026	0.013	0.022	0.800
V(1.59)-9.0-R3	0.149	0.179	0.043	0.021	0.029	2.890
V(1.59)-9.0-R4	0.156	0.168	0.042	0.022	0.035	5.620
Apparent TOFs [s ⁻¹]						
Catalyst	TOF _{C₃H₈}	TOF _{O₂}	TOF _{C₃H₆}	TOF _{H₂}	TOF _{CO₂}	TOF _{CO}
V(0.19)-1.5-R4	4.36E-03	9.24E-03	5.90E-04	3.90E-08	2.98E-03	5.65E-04
V(1.30)-1.5-R1	1.50E-03	1.62E-03	1.01E-04	0.000	5.11E-04	8.92E-05
V(1.30)-1.5-R2	3.52E-03	8.95E-03	4.05E-04	8.74E-08	2.77E-03	7.04E-04
V(0.76)-3.8-R1	9.59E-03	3.25E-02	1.41E-03	2.15E-07	1.14E-02	1.57E-03
V(0.76)-3.8-R2	1.70E-02	5.48E-02	2.26E-03	5.00E-07	1.83E-02	2.79E-03
V(0.19)-9.0-R4	1.51E-02	4.07E-02	1.81E-03	0.00E+00	1.51E-02	9.04E-04
V(1.59)-9.0-R1	2.33E-02	5.18E-02	6.13E-03	2.83E-07	1.37E-02	6.60E-03
V(1.59)-9.0-R2	1.39E-02	3.16E-02	3.16E-03	1.15E-07	7.47E-03	3.74E-03
V(1.59)-9.0-R3	1.31E-02	3.16E-02	2.59E-03	2.55E-07	7.63E-03	3.63E-03
V(1.59)-9.0-R4	1.81E-02	3.89E-02	4.08E-03	6.51E-07	9.69E-03	5.14E-03

Figure S1. Standard (i.e. $p = 1.0 \text{ bar}$) free reaction Gibbs energy as a function of temperature for a set of reactions occurring during propane oxidation.

Figure S2. **a)** NaOH titration curve for the Na-SiO₂ support; **b)** Species diagram of SiO₂ in solution vs pH -built with freeware available at: <http://faculty.chem.queensu.ca/...>; **c)** XPS spectra from the Na 1s region of the support before (i) and after sodium removal (ii).

Figure S3. Scanning electron micrographs for samples of the synthesized materials. The samples were directly introduced to the instrument from the ambient. The nomenclature of the materials is V(y)-z. Where, y = is the wt.% of vanadium of the materials as measured by atomic absorption and z is the pH used for the synthesis.

Figure S3. Continuation

Figure S3. Continuation

The XRD patterns recorded for the hydrated catalysts are shown in **Figure S4**. All patterns were dominated by the wide peak at $\sim 23^\circ$ from the amorphous Na-SiO₂ support and presented a diffraction peak at $\sim 12.6^\circ$. For the sample from V(1.30)-1.5 three additional peaks were recorded at ~ 27.2 , 29.5 , and 50.4° . Among these peaks, the sample from V(1.59)-9.0 did not show the one at $\sim 50^\circ$, while the sample from V(0.76)-3.8 showed none of them. The recorded peaks can be ascribed to sodium vanadate polymorphs of the pyrovanadate type,^{36,37} with chemical formulas such as: α - and β -Na₄V₂O₇ and Na_{1.1}V₃O_{7.6}. The interference of the broad peak of amorphous Na-SiO₂ did not allow the identification of the crystalline phases, nonetheless. Furthermore, the recorded XRD pattern may also be overlapped with that of parent mixed Na,V,Al oxide phases; such as the likes of hughesite, Na₃Al(V₁₀O₂₈)•22H₂O,³⁸ and whose presence was hinted by SEM-EDS.

Figure S4. XRD patterns for selected samples of hydrated V(1.30)-1.5, V(0.76)-3.8, and V(1.59)-9.0.

Figure S5. Measured N₂ physisorption isotherms and BJH pore size distributions, assuming cylindrical geometry, for samples of (a) Na-SiO₂, (b) V(0.19)-1.5, (c) V(0.76)-3.8, (d) V(1.30)-1.5, (e) V(1.59)-9.0, and (f) V(0.19)-9.0.

Figure S6a. Raman spectra for replicas of samples of (a) hydrated and (b) dehydrated: V(1.30)-1.5, V(0.19)-1.5, V(0.76)-3.8, V(0.19)-9.0 and V(1.59)-9.0, and for a sample of dehydrated Na-SiO₂, for reference purposes. Nomenclature: V(x)-y. Where, x = nominal vanadium loading, mol.%, and y = impregnation pH.

Figure S6b. Raman spectra comparison by the zone where the Raman analysis is taken, for samples: V(1.30)-1.5, V(0.76)-3.8 and V(1.59)-9.0.

Figure S6c. Raman spectra of reference materials: VO_x/SiO_2 benchmark and V_2O_5 bulk. Comparison between hydrated and dehydrated states.

Figure S7. Normal probability plots for assessing the stability of the position of the core lines C 1s and Si 2p for the samples measured by XPS.

The media of the relative molar percentage of adventitious carbon for the Na-SiO₂ support was 2.37 ± 0.67 %, Table S3, which is much lower than the typical values found for other oxides.^{39–41} This detail is important because the signal from the C 1s core line was very weak and its binding energy was more unstable than the one recorded for both the Si 2p and O 1s core lines, **Figure S7**. Thus, C 1s was discarded for calibrating the binding energy scale of the spectra. Among Si 2p and O 1s, Si 2p showed ca. half the standard error (i.e. Standard

deviation/ $\sqrt{\text{number of data}}$), ~ 0.022 , of the latter, ~ 0.041 . Therefore, the Si 2p core line was selected for correcting the binding scale of the spectra. The calibration binding energy for Si 2p was set at 103.52 eV which is the average binding energy of the Si 2p and Si 2p_{3/2} core lines for 97 samples of SiO₂ collected in the NIST database.⁴²

Figure S8a. High resolution XPS spectra recorded for the catalysts, **V(0.19)-1.5**, sample 1.

Figure S8b. High resolution XPS spectra recorded for the catalysts, **V(0.19)-1.5**, sample 2.

Figure S8c. High resolution XPS spectra recorded for the catalysts, **V(0.19)-1.5**, sample 3.

Figure S8d. High resolution XPS spectra recorded for the catalysts, **V(0.19)-1.5**, sample 4.

Figure S8e. High resolution XPS spectra recorded for the catalysts, **V(0.19)-1.5**, sample 5.

Figure S8f. High resolution XPS spectra recorded for the catalysts, **V(1.30)-1.5**, replicate 1.

Figure S8g. High resolution XPS spectra recorded for the catalysts, **V(1.30)-1.5**, replicate 2.

Figure S8h. High resolution XPS spectra recorded for the catalysts, **V(1.30)-1.5**, sample 3.

Figure S8i. High resolution XPS spectra recorded for the catalysts, **V(1.30)-1.5**, sample 4.

Figure S8j. High resolution XPS spectra recorded for the catalysts, **V(0.76)-3.8**, sample 1.

Figure S8k. High resolution XPS spectra recorded for the catalysts, **V(0.76)-3.8**, sample 2.

Figure S8I. High resolution XPS spectra recorded for the catalysts, **V(0.76)-3.8**, sample 3.

Figure S8m. High resolution XPS spectra recorded for the catalysts, **V(0.19)-9.0, sample 1.**

Figure S8n. High resolution XPS spectra recorded for the catalysts, **V(0.19)-9.0**, sample 2.

Figure S8o. High resolution XPS spectra recorded for the catalysts, **V(0.19)-9.0**, sample 3.

Figure S8p. High resolution XPS spectra recorded for the catalysts, **V(1.59)-9.0**, sample 1.

Figure S8q. High resolution XPS spectra recorded for the catalysts, **V(1.59)-9.0**, sample 2.

Figure S8r. High resolution XPS spectra recorded for the catalysts, **V(1.59)-9.0**, sample 3.

Figure S8s. High resolution XPS spectra recorded for the catalysts, **V(1.59)-9.0**, sample 4.

Figure S8t. High resolution XPS spectra recorded for the catalysts, **V(1.59)-9.0**, sample 5.

Figure S9. Main effects, a) and b), and interaction, c) and d), plots for assessing the effects of pH and concentration of vanadium in the impregnating solution $-[V]_{Sol}-$ over the concentration of exposed vanadium in the V(x)-y catalysts as measured from oxygen chemisorption. Nomenclature: V(x)-y. Where, x = nominal vanadium loading, mol.%, and y = impregnation pH.

Figure S10a. High resolution XPS spectra recorded for sample 1 of the Na-SiO₂ support.

Figure S10b. High resolution XPS spectra recorded for sample 2 of the Na-SiO₂ support.

Figure S10c. High resolution XPS spectra recorded for sample 3 of the Na-SiO₂ support.

Figure S10d. High resolution XPS spectra recorded for sample 4 of the Na-SiO₂ support.

Figure S10e. High resolution XPS spectra recorded for sample 5 of the Na-SiO₂ support.

Figure S10f. High resolution XPS spectra recorded for sample 6 of the Na-SiO₂ support.

Figure S11. Binding energy of the of the V 2p_{3/2} core line as a function of the inverse of the concentration of vanadium as measured by XPS for the V(x)-y catalysts. Nomenclature: V(x)-y. Where, x = nominal vanadium loading, mol.%, and y = impregnation pH.

Figure S12. Correlation between the concentration of vanadium at the surface assessed by XPS and the concentration of exposed vanadium sites assessed by O₂ chemisorption.

Figure S13. Correlation between the binding energy of the of the V 2p_{3/2} core line and the surface Na/V molar ratio assessed by XPS.

Figure S14. Results from a catalytic test performed with the Na-SiO₂ support. Reaction conditions: propane GHSV = 4 h⁻¹, feed composition = 5:10:115 [mL NTP /min] C₃H₈:O₂:N₂, p = atmospheric pressure (Bucaramanga ~ 0.89 bar).

Figure S14. Continuation.

Figure S14. Continuation.

Figure S15. (a) Evolution of reactants fractional conversion, (b) products fractional yields, and (c) selectivity as a function of time on stream and temperature for the VO_x/SiO_2 benchmark. Reaction conditions: propane GHSV = 4 h^{-1} , feed composition = 5:10:115 [mL NTP /min] $\text{C}_3\text{H}_8:\text{O}_2:\text{N}_2$, p = atmospheric pressure (Bucaramanga $\sim 0.89 \text{ bar}$).

Figure S15. Continuation

Figure S16. Selectivity as a function of conversion for the catalysts based on sodium metavanadates, **a) – c)**, and for the VO_x/SiO₂ benchmark. Reaction conditions: T = 350 – 500 – 350°C for **a)**, **b)**, and **c)**; T = 350 – 550 – 350°C for the benchmark, **d)**, propane GHSV = 4 h⁻¹, feed composition = 5:10:115 [mL NTP /min] C₃H₈:O₂:N₂, *p* = atmospheric pressure (Bucaramanga ~ 0.89 bar).

Figure S17. Selectivity as a function of conversion for the catalysts based on sodium metavanadates, **a) – c)**, and for the VO_x/SiO_2 benchmark. Reaction conditions: $T = 350 - 500 - 350^\circ\text{C}$ for **a)**, **b)**, and **c)**; $T = 350 - 550 - 350^\circ\text{C}$ for the benchmark, **d)**, propane GHSV = 4 h^{-1} , feed composition = 5:10:115 [mL NTP /min] $\text{C}_3\text{H}_8:\text{O}_2:\text{N}_2$, p = atmospheric pressure (Bucaramanga ~ 0.89 bar).

Figure S18. Interaction plots for assessing the non-additive effects of pH and vanadium concentration in solution over the apparent propane and oxygen turnover rates during the oxidation of propane. Reaction conditions: Propane GHSV = 4 h⁻¹, 500°C, feed composition = 5:10:115 [mL NTP /min] C₃H₈:O₂:N₂, *p* = atmospheric pressure (Bucaramanga ~ 0.89 bar).

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