Characterization of surface species on V / SiO_2 and V,Na / SiO_2 and their role in the partial oxidation of methane to formaldehyde

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Silica-supported vanadium (1–8 wt%) and vanadium (5 wt%)–sodium (0.4 wt%) catalysts have been characterized by laser Raman spectroscopy, temperature-programmed reduction, X-ray photoelectron spectroscopy, NO + NH_3 rectangular pulses and oxygen chemisorption. The presence of different vanadium species was correlated with activity and selectivity during the methane partial oxidation reaction. The pre-impregnation of the silica support with sodium favors vanadium dispersion, but strongly diminishes V=O concentration due to the formation of orthovanadate-like compounds. As a result of these modifications, methane conversion is strongly inhibited while formaldehyde decomposition is favored.

Keywords: vanadium surface species; silica-supported catalysts; methane partial oxidation; sodium poison; V=O sites

1. Introduction

Supported vanadium catalysts have been extensively studied for their application in the selective oxidation of hydrocarbons [1]. V / SiO_2 has received special attention in the last few years for its ability to oxidize methane to formaldehyde [2]. Several groups have tried hard to find the link between active sites on V / SiO_2 and their role in the reaction mechanism of this selective oxidation. Among them, Koranne et al. [3] using transient methods suggested that the oxygen from the lattice participates in the reaction. Kartheuser and Hodnett [4] correlated the dispersion of vanadium oxide on silica with the selectivity to formaldehyde. They concluded that the size of V_2O_5 crystallites determines the selectivity. We have recently reported [5] that the formaldehyde yield correlates with the vanadyl (V=O) concentration on the catalyst surface.

Deo and Wachs [6] thoroughly characterized V_2O_5 supported on several oxides. In the case of hydrated V / SiO_2 they detected the presence of decavanadates, metavanadates and V_2O_5 whose proportions vary with the vanadium load. In dehydrated solids only monomeric species and V_2O_5 were detected. Somorjai and coworkers [7] studied different loaded V/silica catalysts by oxygen chemisorption and laser Raman spectroscopy. They developed a method for measuring the active surface area of supported and unsupported V_2O_5 following reduction in hydrogen.

Despite these important efforts, the role played by the different vanadium containing species in the oxidation of methane to formaldehyde is not clearly understood. The addition of alkaline metals which poison the selective oxidation reaction on both Mo/ and V / SiO_2 [8] may help understand the connection between active sites and selectivity. Bañares et al. [9] produced interesting results by studying the effect of Na, K and Cs upon the catalytic behavior of Mo / SiO_2.

In this work, we report results on the characterization of surface species present in V / SiO_2 and Na,V / SiO_2 using laser Raman spectroscopy (LRS), X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR), oxygen chemisorption, and NO+NH_3 rectangular pulses (NARP). The data obtained are interpreted in terms of the catalytic behavior in a flow reactor during the selective oxidation of methane to formaldehyde.

2. Experimental

A commercial non-porous silica Cabot M5 Aerosil – particle size 5–30 Nm, BET area 200 $m^2 g^{-1}$ and composition $SiO_2 > 99.8\%$, Al < 5 ppm, Fe < 2 ppm, and Na < 0.5 ppm – was used as a carrier. This was impregnated during 12 h with aqueous solutions in appropriate amounts so as to yield solids with 1–8 wt% vanadium. The impregnated solids were dried at 393 K and calcined 2 h at 473 K and 12 h at 873 K. The metal salts used for the impregnations were Merck pro-analysis ammonium vanadate and sodium hydroxide. The amount of metal loading is defined as the ratio of the weight of metal divided by the total weight of the catalyst on a percent basis. The vanadium–silica catalysts are denoted in the text by the loading figure preceding V / SiO_2. Catalysts containing sodium as well, were prepared by washing the silica support with 0.01 N sodium hydroxide, drying it prior to vanadium impregnation. This vanadium–

sodium–silica catalyst, which contains 5 wt% of vanadium and 0.4 wt% of sodium, is denoted in the text as 5% V,Na/SiO_2.

The BET area of each catalyst was measured after calcination but prior to reaction using a Micrometrics Accusorb 2100 sorptometer. The XPS spectra were obtained at room temperature with an ESCA 750 computer driven, Shimadzu instrument, using Mg Kα radiation. The V/Si, Na/Si and V/O atomic ratios were calculated using the area under the Si 2p, V $2p_{3/2}$, Na 1s and O 1s peaks, the Scotfield photoionization cross-sections, the mean free paths of the electrons and the instrument function which was given by the ESCA manufacturer. The binding energies (BE) were always referred to C 1s at 284.6 eV. The V $2p_{1/2}$ intensity was not considered in the calculation of vanadium surface concentration due to the overlapping of this signal with the O 1s ghost [10].

Oxygen chemisorption experiments were performed in order to estimate the vanadium dispersion in V/SiO_2 and V,Na/SiO_2 catalysts. The technique used was that developed by Oyama et al. [7], which consists in reducing the surface with hydrogen at 640 K and measuring oxygen chemisorption at the same temperature.

The surface of vanadium–silica and vanadium–sodium–silica catalysts was also characterized using the technique developed by Satsuma et al. [11] for bulk V_2O_5 which was used by Kartheuser and Hodnett [4] to measure vanadium oxide dispersions on V/SiO_2 catalysts. This technique, named NARP (nitric oxide plus ammonia rectangular pulses), consists in monitoring the nitrogen response from the NO plus NH_3 pulses. The area under the initial sharp peak of nitrogen is assigned to the amount of V=O sites present on the surface with a stoichiometry N_2/V=O equal to unity, while the tail side corresponds to the reoxidation of the surface sites with the oxygen coming from the bulk. These experiments were typically performed after calcination and degassing with He (100 cm^3/min) at 400°C during 2 h, using 0.02 g of catalyst and a 3 min long rectangular pulse of NO (0.1%) + NH_3 (2%).

Temperature-programmed reduction experiments were carried out using 0.08 g of sample which was pretreated in situ at 873 K during 2 h in dry oxygen. Following pretreatment, the samples were cooled to room temperature and the gas switched to 5% hydrogen in argon mixture. The gas flow was 25 cm^3/min and the temperature was raised at 10 K/min to 1073 K.

The LRS (laser Raman spectroscopy) was performed using a JASCO TRS-600SZ-P single monochromator spectrophotometer equipped with an intensified photodiode array cooled to about −120°C with liquid N_2. The excitation source, used to obtain the spectra, was the 514.5 nm line of a Spectra 9000 Photometrics Ar ion laser. The laser power, measured at the samples, was set at 30–40 mW. All the spectra were recorded with the samples under ambient conditions.

Steady-state kinetic experiments were performed using a single-pass flow reactor made of fused silica with an inside diameter of 1.8 cm and a heated length of 15 cm. In order to minimize formaldehyde oxidation in the gas phase, the diameter of the gas outlet tube was diminished to 0.1 cm immediately after the reaction zone. The reactor was loaded with 0.2 g of catalyst, and the total flow rate (methane plus oxygen) was 17 cm^3/min, with a CH_4/O_2 ratio of 9. Typically, methane conversions and formaldehyde selectivities were measured between 793 and 973 K. Matheson Specialty Gases with the following purities were used: CH_4 (99.99%), O_2 (99.96%) and He (99.995%). Analyses of the feed and reactor effluent streams were performed by gas chromatography using a thermal conductivity detector. A Porapak T column was used to separate formaldehyde, carbon dioxide and water, and a molecular sieve 5A column for methane, oxygen and carbon monoxide.

3. Results and discussion

3.1. *NARP, oxygen chemisorption, and TPR characterization*

We have used three techniques in order to cross-check data about the extent of surface exposure of vanadium in V/SiO_2 and V,Na/SiO_2 catalysts. Table 1 shows dispersion data calculated from the NARP technique and oxygen chemisorption. TPR dispersion data calculated from the area of the low-temperature peak divided by the total TRP area [12] are shown in fig. 1.

Kartheuser and Hodnett [4] have reported dispersion values between 0.3 and 0.1 (NARP technique) for a series of catalysts loaded with 1–8% vanadium on silica, similar to the data shown in the first column of table 1. Oyama et al. [7] reported dispersion values calculated from O_2 chemisorption higher than those shown in table 1. A possible explanation for the discrepancy between both sets of values is the different starting vanadium salt; they used vanadium oxalate for impregnation while we used ammonium metavanadate.

In any case, the dispersion values calculated with different techniques follow the same pattern of variation with loading. A special analysis requires the solid with Na (table 1). The NARP technique shows an over 15 times decrease in dispersion upon Na addition while the other techniques show significant increases. XPS data (table 1) also show the same trend. This requires further investigation at the molecular level to understand the nature of the interaction of sodium with the supported vanadium moieties (vide infra).

Fig. 1 shows the TPR profiles of solids with and without sodium. The shape of the 5% V/SiO_2 curve is similar to those reported by Koranne et al. [12]. The lowest temperature peak (~ 370°C) is assigned to the reduction of surface vanadium species. This temperature is very close

Table 1

Vanadium dispersion, TPR data, and XPS analysis of V/SiO_2 and V,Na/SiO_2 catalysts

Catalyst	Dispersion of vanadia		$(V/Si)_s$ [c]	Na 1s [d] (Eb)	Reduction [e] (%)	Average oxidation state [e]
	NARP	Chemisorption of O_2				
1%V/SiO_2	0.24 [a]	0.31 [b]	0.012	–	60	3.8
1.6%V/SiO_2	0.25	0.21	0.015	–	65	3.7
2.5%V/SiO_2	0.29	0.25	0.017	–	63	3.7
5%V/SiO_2	0.22	0.16	0.020	–	61	3.8
8%V/SiO_2	0.15	0.09	0.025	–	59	3.8
5%V,Na/SiO_2	< 0.01	0.30	0.035	1070.9	70	3.6
$NaVO_3$ [f]	–	–	–	1070.9	–	–

[a] V=O sites/mol of V_2O_5 [4,12].

[b] Mol of O_2 chemisorbed/mol of V_2O_5 [7].

[c] Surface vanadium/silicon atomic ratio measured by XPS.

[d] Sodium binding energy.

[e] From TPR data.

[f] Merck pro-analysis as received.

to the value reported by Oyama et al. [7] for the reduction of surface species. The peaks at the higher temperatures pertain to the bulk reduction of the vanadium species which is only 60–70% complete at 700°C. This is in agreement with the data reported in ref. [12]. Although the TPR profile of the sodium containing catalysts is also made up of three peaks, the lowest temperature signal is now more important. This is consistent with the higher dispersion of this sample compared to the Na-free 5% catalyst.

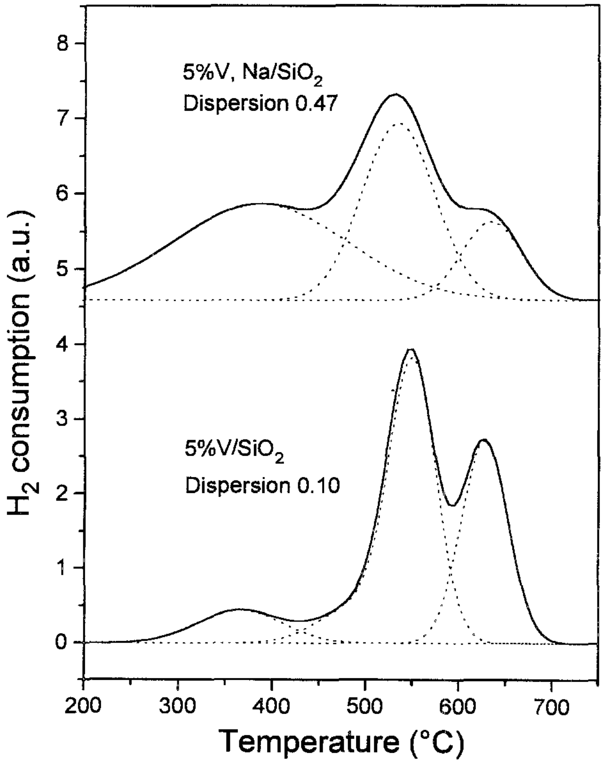

Fig. 1. The effect of sodium on V/SiO_2 thermograms. Dispersion values were calculated dividing the area of peak at lower temperature by the total TPR area [12].

3.2. Raman characterization

The laser Raman spectra of the V/SiO_2 samples containing 1.6 and 5% vanadium, with and whithout Na, are shown in fig. 2. Although the spectra of the other catalysts reported in table 1 were also recorded, they are not reproduced here because they are very similar to those reported by Oyama et al. [7].

The assignment of the main peaks observed in the spectra are reported in table 2. It is accepted that the band at 1035 cm^{-1} is due to the stretching mode of the terminal V=O bond of monomeric vanadyl species directly bound to the support [7,13–15]. The broad band between 990 and 940 cm^{-1} and the one at around 600 cm^{-1} may be due to the presence of octahedrally coordinated vanadium species in a decavanadate-like environment [6,14,16]. The signals between 135 and 995 cm^{-1}, observed in the samples containing 2.5% of vanadium or more, may be all attributed to crystalline V_2O_5 [7,14,17]. The strong peak at 995 cm^{-1} is due to the stretching mode of the terminal V=O bond, while the bands between 800 and 500 cm^{-1} (fig. 2) are usually assigned to stretching modes of bridging V–O–V bonds. Finally, those bands appearing below 450 cm^{-1} have been attributed to bending and symmetry related Raman modes due to medium and long-range order influence [14,17].

On the basis of these results, it may be said that three different species are present on the V/SiO_2 catalysts prepared in this work: monomeric vanadyl species, decavanadate-like polymeric moieties and crystalline V_2O_5. As the V load in the catalysts decreases, the following trends are observed: (1) The ratio of intensities of the bands at 1035 and 995 cm^{-1}, defined as $I(1035)/I(995)$, increases; (2) the strong band at 135 cm^{-1}, assigned to long-range order influence, becomes less intense and broader, fading out at loads of 1.6% of vanadium. This last fact is indicating that for loads higher than 1.6%, crystalline V_2O_5 is already present on the catalyst surface.

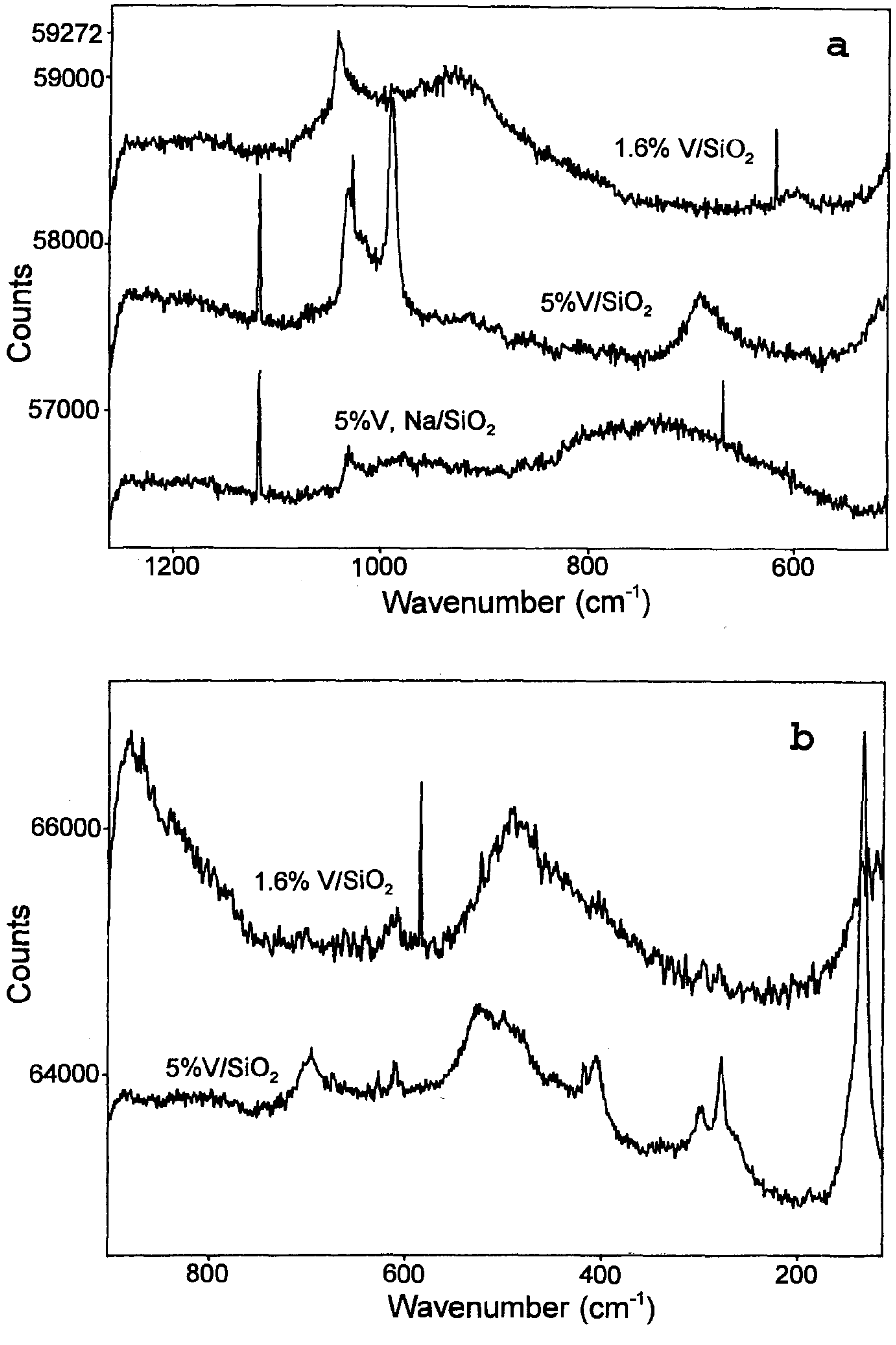

Fig. 2. Laser Raman spectra of V/SiO_2 catalysts with and without Na. Spectra were taken at ambient conditions.

It has been established that the monomeric vanadyl species has a highly distorted tetrahedral structure with one very short terminal V=O bond of length 1.583 Å and a bond order of 2.0 [14,18]. On the other hand, Hardcastle and Wachs have estimated that for the three bridging V–O–support bonds, where the support is Al_2O_3, the V–O bond length may be roughly 1.78 Å [14]. For the case of SiO_2, these values may be different. Nevertheless, according with data reported in the literature, they may be taken as a good approximation to describe the distorted tetrahedral structure of these species on the SiO_2 support [19]. On this basis it is concluded that these monomeric species have vanadyl character.

The polymeric moieties are probably decavanadate-like species in which vanadium is in octahedral coordination. This assumption is supported by the work of Deo and Wachs [6]. They found that the species formed on the surface of different supports strongly depend on the pH at pzc of them. For the case of SiO_2, the pH at pzc is 3.9. According to the corresponding phase equilibrium diagram, at low concentrations and for this pH, the main species in solution are $(V_{10}O_{26}(OH)_2)_4$– and $VO(OH)_3)$–

Table 2
Band assignments in LR spectra of V/SiO_2 and V,Na/SiO_2

Catalyst	Monomeric vanadyl species	Octahedrally coordinate vanadium species		Crystalline V_2O_5		
	1035 cm^{-1}	990–940 cm^{-1}	600 cm^{-1}	995 cm^{-1} [a]	697 cm^{-1}	135 cm^{-1} [b]
1% V/SiO_2	main	broad band	weak	–	–	–
1.6% V/SiO_2	main	broad band	weak	–	–	–
2.5% V/SiO_2	main	–	–	weak	–	weak
5% V/SiO_2	strong	–	–	strong	strong	strong
8% V/SiO_2	strong	–	–	strong	strong	strong
5% V,Na/SiO_2 [c]	weak	–	–	–	–	–

[a] Due to the stretching mode of terminal V=O [7,14,17].
[b] Assigned to long-range order influence [7,14,17].
[c] A broad band also observed between 600 and 800 cm^{-1}.

in agreement with the assignment done above. The dehydration of these species would lead to the formation of the highly distorted monomeric tetrahedral species directly bonded to silica and some clusters of polymeric species with vanadium in an octahedral environment, which would also be the species present under reaction conditions. The presence of polymeric species have also been reported for vanadium supported on both silica and alumina under dehydrated conditions [15,20]. The formation of this decavanadate-like species may be related to the preparation method [21] and can explain the low dispersion values obtained in this work.

Deo and Wachs [6], recording the spectra at ambient conditions and with low laser power (2 mW), detected only polymeric species of the decavanadate type. In this work, the samples are also at ambient conditions, but the species formed on the support surface are easily dehydrated due to the high laser power used (around 30 mW on the sample) and the weak vanadium compounds–support interaction. This may explain the appearance of the 1035 cm^{-1} band assigned to monomeric species.

Valuable information is obtained when the support is treated with a very small quantity of sodium. The main and sharp peaks due to crystalline V_2O_5 at 995, 697 and 135 cm^{-1} are not observed any more and very broad and weak bands between 970 and 600 cm^{-1} appear instead (fig. 2a). In fact the broad band between 600 and 800 cm^{-1} is now the most intense. A similar spectrum was found for the case of V/(delta-theta)Al_2O_3 [16]. On the basis of a preliminary XANES study, it was suggested that the main species on the Al_2O_3 surface are tetrahedral monomers. The formation of this new monomeric species was attributed to the presence of alkaline (Na, K) impurities on the support surface [18].

These observations are in agreement with the higher dispersion values obtained by TPR and O_2 chemisorption when sodium is added to the V/SiO_2 catalysts (fig. 1 and table 1). On the other hand, it has been reported that the main signal of vanadate ions in solution appears around 800 cm^{-1} [20]. In other words, it may be said that sodium addition leads to the redispersion of the V_2O_5 crystallites on the SiO_2 surface, tetrahedral monomers being now the main species. Thus, the broad feature between 600 and 800 cm^{-1} may be due to vanadate-like isolated tetrahedron, i.e., orthovanadate-like species. Sodium metavanadate species may also be present according to the XPS data (last two rows of table 1). The formation of these orthovanadate-like isolated tetrahedra and metavanadate clusters may be explained by taking into account a change of the pH at pzc due to the sodium hydroxide addition to the silica support [6]. Thus, the sodium-modified silica surface would have a pH at pzc similar to that of basic oxides like MgO. The surface vanadium species observed on MgO are orthovanadate ($(VO_4)^{3+}$), pyrovanadate ($(V_2O_7)^{4-}$) and metavanadate clusters ($(VO_3)_n^-$) in agreement with the corresponding phase equilibrium diagram [6] and with the results obtained by LRS and XPS (fig. 2a and table 1). Since sodium loading is low (0.4 wt%), a considerable amount of vanadium is not combined with Na. Results suggest that sodium is mainly consumed to form surface $NaVO_3$-like compounds, in agreement with XPS results, and the remaining vanadium is in the form of tetrahedral monomers directly bond to the modified silica surface.

Orthovanadates are non-distorted tetrahedra with low or none vanadyl nature. The four V–O bonds are almost equivalent in this family of compounds, with very similar bond orders and lengths. For instance, Na_3VO_4 has one bond of 1.68 Å and three of 1.70 Å in length with bond orders of 1.40 and 1.32, respectively [6]. However, according to the Raman shifts observed for the 5% V,Na/SiO_2 sample (fig. 2a), it is more likely that the bond lengths and orders are closer to those of $BiVO_4$, i.e., 1.7–1.8 Å and 1.1–1.3, respectively [14]. The broad band is probably due to both the diversity of V–O bonds in this tetrahedral monomer and laser heating. These bond orders are quite different from 2.0, supporting the idea of the low vanadyl character of this species.

Metavanadates possess a somehow more important vanadyl nature than orthovanadate species [6]. The former seem to be in a much lower concentration on the sodium modified surface since they are not detected in the Raman spectrum in agreement with the low value of

V=O sites/gmol of V_2O_5 obtained for the sodium modified sample (table 1). The NARP technique is based on the fact that V=O groups are selectively reduced by the NO–NH_3 mixture.

3.3. *The role of surface species in the selective oxidation of methane*

Table 3 shows catalytic data for all the catalysts reported in table 1. Increasing vanadium content results in higher conversions of methane and lower selectivities to formaldehyde. Note that upon Na addition (last row) both conversion and selectivity are the lowest of them all.

Fig. 3 shows the effect of V=O concentration measured by the NARP technique [5] upon the turnover frequency (TOF) calculated on the basis of the same sites. The TOF of the sample containing Na does not fit in the curve.

Irusta et al. [5] showed that V=O sites play a key role in the oxidation of methane to formaldeyde. They found that the addition of sodium leads to the decrease of V=O site concentration sharply reducing the catalytic activity. Bañares et al. [9] studied the effect of Na, K, and Cs addition to Mo/SiO_2. They concluded that the decrease in activity is due to a significant lowering in the surface concentration of isolated Mo moieties. They did not explain, however, how the decomposition of formaldehyde to carbon monoxide may be affected by the presence of alkaline metals.

The results shown in table 3 indicate that the methane conversion increases with the V=O site concentration while the formaldehyde yield reaches a maximum between 0.037 and 0.070 mmol V=O/g cat. This range corresponds to vanadium loads of 1.6–2.5%. For these and lower loads, the main species detected by LRS was the highly distorted tetrahedral monomer directly bonded to the SiO_2 surface. The selective oxidation of methane in formaldehyde is favored by the presence of this vanadyl species. On the other hand when the presence of crystalline V_2O_5 becomes important in the V/SiO_2 catalyst, i.e., for vanadium loads of 2.5% or more, the selectivity to formaldehyde dramatically drops. This is clearly seen in catalysts with 5 and 8% of vanadium, which present very different selectivities for the same conversion (table 3).

These two vanadium species, detected by LRS before any sodium addition to the support, have a definite vanadyl character. They possess a very short terminal V=O bond with bond orders in the range of 1.8–2.0. After sodium addition, the almost total disappearance of these two species was observed. Instead, the main species was now a non-distorted tetrahedral vanadate with very low or none vanadylic nature. The sodium modified catalyst proved to be much less active and selective to formaldehyde than the non-modified ones. This effect might be related to the formation of the highly dispersed orthovanadate-like phase able to catalyze the decomposition of formaldehyde but not the methane oxidation.

Thus, it seems that the most important difference between the species detected in each case is the presence or not of very short terminal V=O bonds. Species having this unique feature play a key role in the selective oxidation of methane to formaldehyde. Species whithout terminal V=O bonds are not active and selective for this reaction. Thus, it may be concluded that in order to attain a vanadium-based catalyst with a high selectivity to formaldehyde in the methane oxidation reaction the presence of species possessing vanadyl nature as the vanadyl monomers and crystalline V_2O_5 is necessary.

Both monomeric highly distorted tetrahedral species directly bound to the silica support and V_2O_5 possess terminal V=O and bridging V–O bonds. However, the presence of crystalline V_2O_5 significantly decreases the formaldehyde yield (table 3). In order to explain these results, a mechanism similar to that suggested for the case of oxidative dehydrogenation of propene may be proposed [22].The V=O group present in both species would be responsible for the initial hydrogen abstraction. This is supported by the fact that the vanadate species formed on the V,Na/SiO_2 is not active for methane oxidation to formaldehyde and the probable reason for this is that this species cannot abstract the hydrogen.

Fig. 3 shows a steady decay of both formaldehyde

Table 3
Catalytic behavior in methane oxidation to formaldehyde

Catalyst	S_g[a] (m^2/g)	C[b]	S[c]	Y[d]	V=O/g cat.	TOF_{CHOH}[e]	TOF_{CH_4}[f]
1% V/SiO_2	177	0.031	0.35	0.011	0.023	2.50	7.14
1.6% V/SiO_2	177	0.046	0.28	0.013	0.037	1.80	6.40
2.5% V/SiO_2	176	0.055	0.22	0.012	0.070	0.90	4.10
5% V/SiO_2	132	0.069	0.15	0.010	0.110	0.47	3.10
8% V/SiO_2	121	0.068	0.08	0.005	0.120	0.24	3.00
5% V,Na/SiO_2	64	0.020	0.07	0.001	0.007	0.52	7.40

[a] Surface area.

[b] Methane conversion.

[c] Formaldehyde selectivity.

[d] Formaldehyde yield $Y = CS$.

[e] Mole of formaldehyde produced per second per V=O site.

[f] Mole of methane converted per second per V=O site.

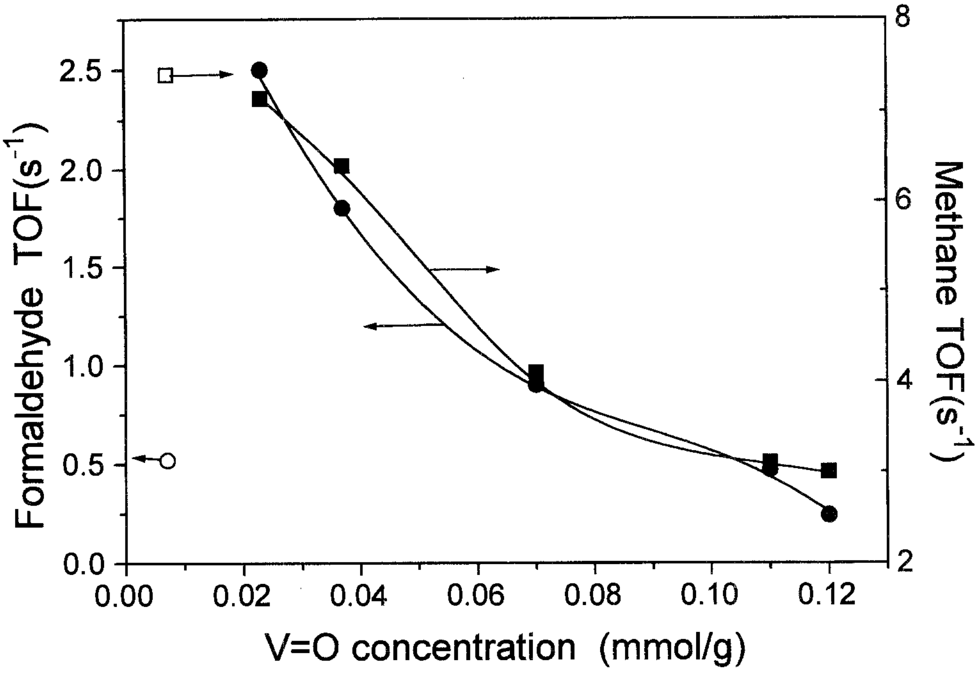

Fig. 3. Effect of V=O concentration on the catalytic behavior. (○, □) V,Na/SiO$_2$; (●, ■) V/SiO$_2$. Reaction conditions: $T = 500$°C, total flow rate 17 cm^3/min, CH$_4$/O$_2$ = 9, 0.2 g of catalyst.

and methane TOFs which is consistent with the changing proportion of at least two different kinds of V=O containing species detected on this catalyst (fig. 2, table 2).

The bridging oxygen V–O–V, in the case of crystalline V_2O_5, or V–O–Si, in the case of monomers directly bound to the support surface, would also participate in the reaction under study. Since V_2O_5 has longer V–O bridging bonds than the monomeric species directly bound to the support, it would be expected that the bridging oxygen from V_2O_5 were more easily removed than the one from the monomers. This fact can favor deep oxidation reactions, thus explaining the higher activity and lower formaldehyde yield as the concentration of crystalline V_2O_5 species increases. On the other hand, the bridging oxygens in the non-distorted tetrahedral monomers could interact with formaldehyde to give carbon monoxide and water thus explaining the low selectivity to formaldehyde when orthovanadate-like species are present on the SiO_2 modified surface.

4. Conclusions

The effect of sodium addition upon the catalytic behavior may now be explained by the formation of non-distorted orthovanadate-like tetrahedra with very low or none vanadyl character. This vanadate species possesses four almost equivalent V–O bonds, i.e., similar V–O bond lengths and orders. Thus, there is not a short terminal V–O bond in this type of compounds and the methane molecule cannot be activated through H abstraction, thus explaining the low activity of the non-distorted vanadate monomers. On the other hand, this species can decompose the formaldehyde to carbon monoxide, thus explaining the low selectivity of the sodium modified catalyst.

Highly distorted tetrahedral monomers directly bonded to the support surface are the active species for the selective oxidation of methane to formaldehyde. These species possess both a short terminal V=O bond and an ideal bridging V–O length. The formation of crystalline V_2O_5 leads to an important drop of selectivity to formaldehyde, probably due to the most labile bridging oxygen present in the highly distorted octahedra.

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