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Chemical and structural characterization of V₂O₅/TiO₂ catalysts

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A series of V₂O₅/TiO₂ samples was synthesized by sol-gel and impregnation methods with different contents of vanadia. These samples were characterized by x-ray diffraction (XRD), Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), and electronic paramagnetic resonance (EPR). XRD detected rutile as the predominant phase for pure TiO₂ prepared by the sol-gel method. The structure changed to anatase when the vanadia loading was increased. Also, anatase was the predominant phase for samples obtained by the impregnation method. Raman measurements identified two species of surface vanadium: monomeric vanadyl (V⁴⁺) and polymeric vanadates (V⁵⁺). XPS results indicated that Ti ions were in octahedral position surrounded by oxygen ions. The V/Ti atomic ratios showed that V ions were highly dispersed on the vanadia/titania surface obtained by the sol-gel method. EPR analysis detected three V⁴⁺ ion types: two of them were located in axially symmetric sites substituting for Ti⁴⁺ ions in the rutile structure, and the third one was characterized by magnetically interacting V⁴⁺ ions in the form of pairs or clusters. A partial oxidation of V⁴⁺ to V⁵⁺ was evident from EPR analysis for materials with higher concentrations of vanadium. © 2001 American Vacuum Society. [DOI: 10.1116/1.1380720]

I. INTRODUCTION

Vanadia supported on titania constitutes a well-known catalytic system for selective oxidation reactions of o-xylene, ammoxidation of hydrocarbon, and reduction of NO_x with NH₃.¹⁻³ The outstanding catalytic behavior of vanadia supported on titania in comparison with that supported on other oxides, such as SiO₂ or Al₂O₃, is attributed to the strong support-active-phase interaction. Vanadia supported on anatase presents higher activity and selectivity than vanadia supported on rutile. Vejux and Courtine⁴ proposed that a close epitaxial crystallographic match between the structure of the (010) plane of V₂O₅ and the (001) plane of anatase leads to the spreading and preferential exposure of the (010) crystalline active plane. Lietti *et al.*⁵ proposed that the formation of a stable VO_x monolayer over anatase and the similar electronegativities of titanium and vanadium as the main reasons for apparent superior catalytic performance.

There has been a lot of controversy about the nature and functionality of the active sites of these catalysts. However, we believe that the reaction mechanisms involving the surface V⁴⁺/V⁵⁺ redox pair contribute to the activity and selectivity of the V₂O₅/TiO₂ system. This hypothesis has been increasingly adopted in the literature.⁶⁻¹⁰

The great disadvantage of the titania support prepared by conventional ceramic processes is its low specific surface area. In addition, the anatase phase presents poor thermal stability at high temperature. Its partial transformation into rutile is thermodynamically favored but leads to a deterioration of catalytic performance. Then, the characteristics of the support are fundamental for the stabilization of the active phase in the V₂O₅/TiO₂ catalysts and depend mainly on preparation methods. Several synthesis methods have been employed, and of special importance are those in which the active phase is dispersed by aqueous impregnation of soluble salts or by nonaqueous impregnation of alkoxides into the support.¹¹⁻¹³ The main objective of these methods is the maximization of the catalyst effective region formed by the reagent/active-phase/support interface.¹⁴ However, in these impregnation methods, the dispersion, the active-phase concentration, and the textural and structural properties of the catalyst are limited by the characteristics of the support.^{13,15-17}

The sol-gel method has been proposed as an alternative route to synthesize catalysts with a high surface area and a stable active phase.¹⁷⁻²³ This method permits a better control of the textural and structural properties of the catalytic systems, and an improved dispersion of the active phase on the support.^{22,23}

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In this work, we present the results of V_2O_5/TiO_2 catalysts prepared by a modified sol–gel method. The purpose of this investigation is to develop a preparation method capable of maximizing the vanadia dispersion on the titania surface. The conditions that favor the formation of rutile TiO_2 are developed to show the influence of the active phase on the V_2O_5/TiO_2 structural and textural properties. We demonstrate that the active phase permits the control of the textural and structural properties, promoting materials with high surface area and enabling a mixed anatase/rutile support at a low calcination temperature. We have employed x-ray diffractometry (XRD), Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), and electron paramagnetic resonance (EPR) to characterize the V_2O_5/TiO_2 catalysts.

II. EXPERIMENTAL PROCEDURES

TiO_2/V_2O_5 samples with different contents of V_2O_5 (1, 3, 6, and 9 wt %) were synthesized using sol–gel and impregnation methods. The vanadium precursor, NH_4VO_3 , was dissolved in nitric acid to control pH . Solution A was prepared by dissolving NH_4VO_3 in nitric acid ($pH=1$) under 75 W ultrasonic vibrations for 1 min. Solution B was prepared by diluting tetraisopropyl-orthotitanate ($C_{12}H_{28}O_4TiO$) in isopropyl alcohol at a molar ratio of 0.25. After solubilization, solution A was added to solution B and a gel was formed immediately. The gel was then vigorously stirred for 5 min under 75 W ultrasonic vibrations, and after a 24 h rest the resulting gel was dried at 110 °C for 4 h, and calcined at 723 K for 16 h. Catalysts containing 6 and 9 wt % of V_2O_5 were prepared by impregnation of P-25 Degussa TiO_2 (50 m^2/g) in solution A. The solid was gradually dried and calcined in a manner which was similar to the previous method.

X-ray powder diffraction patterns were obtained using an automatic Rigaku Rotaflex diffractometer model RU 200B with $Cu K\alpha$ radiation (40 kV/40 mA, 1.5405 Å) and a nickel monochromator filter.

Raman spectra were obtained with 514.5 nm argon ion laser line, Spectra Physics 2020, a Jobin-Yvon U1000 double monochromator with holographic gratings, and a computer-controlled photon-counting system. The Raman spectra were obtained with an average of 100 scans, a spectral resolution of 4 cm^{-1} at room temperature, and a power excitation of 45 mW.

XPS analysis was performed in ultrahigh vacuum (low 10^{-7} Pa range) using a KRATOS XSAM HS spectrometer. $Mg K\alpha$ ($h\nu=1253.6$ eV) was used as the x-ray source, with a power determined by emission at 15 mA and 15 kV. The high-resolution spectra were obtained with an analyzer pass energy of 20 eV. The samples were flooded with low-energy electrons from a flood gun to avoid charging effects. The binding energies were referenced to an adventitious carbon 1s line set at 284.8 eV. The Shirley background and a least-square routine were used for peak fitting. The sensitivity factors for quantitative analysis were referenced to $S_{F1s}=1.0$.

EPR experiments were carried out using both X and Q bands on powdered samples. All EPR absorption spectra were recorded as the first derivative of absorption at 77 K.

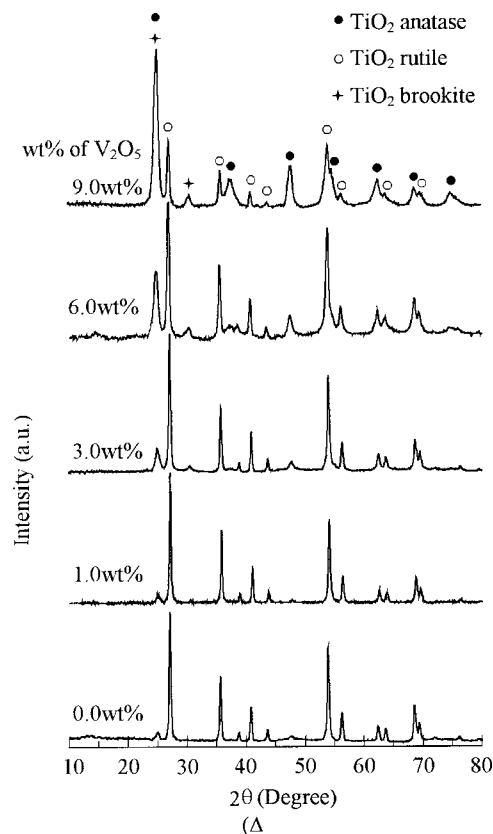


Fig. 1. Evolution of the XRD patterns of V_2O_5/TiO_2 xerogel with the vanadia concentration.

The Q band spectra were taken with an E -line Varian Spectrometer operating at 34 GHz. The X -band (9.6 GHz) spectra were measured using a magnetic-field modulation frequency of 85 kHz. Calibration of g values was based on the $g = 1.9797$ signal of a $MgO:Cr^{3+}$ marker.

III. RESULTS AND DISCUSSION

A. X-ray diffraction

Figure 1 shows the typical XRD peaks attributed to the anatase, rutile, and brookite phases. Peaks associated with crystalline V_2O_5 are not observed for all samples prepared by the sol–gel method, indicating the efficient dispersion of vanadium in the titania matrix.

Lietti *et al.*⁵ showed that the transformation of anatase to rutile is only considered an efficient process for TiO_2 samples calcined at temperatures higher than 973 K. However, the XRD results depicted in Fig. 1 indicate the predominance of rutile for titania calcined at a lower temperature (723 K). This may be the consequence of a decrease in the phase transition temperature of anatase to rutile promoted by the above preparation method. In acidic preparations, the hydrolysis of the titanium alkoxide is faster than the condensation, producing samples with many hydroxyl groups. The thermal treatment of these samples causes dehydroxylation, and forms Vac^+O^{2-} anionic vacancies.²⁴ The high defect concentrations of anatase crystals contribute to the decrease in the anatase to rutile phase transformation.²⁴

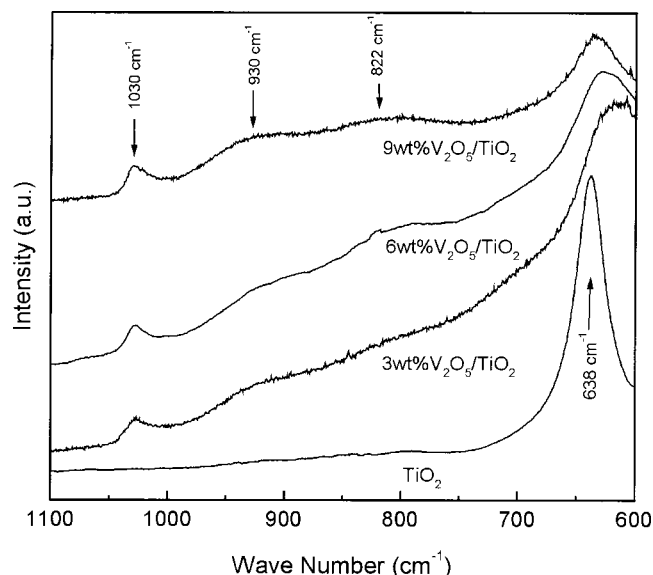


Fig. 2. Raman spectra of the V_2O_5/TiO_2 xerogel dehydrated at 473 K under 10^{-3} Torr pressure.

A substantial increase in the anatase peak intensity is observed as the vanadium loading increases. This can be attributed to the strong vanadium–titanium interaction which inhibits the phase transformation of anatase to rutile. The vanadium atoms can occupy the anionic vacancies, which were formed in the preparation method, and this occupancy contributes to the stabilization of titania in the anatase phase. Similar effects are related to the presence of impurities, such as sulfate and phosphate,⁵ or attributed to a chemical solid interaction between vanadia and anatase.²⁵

In short, the structural nature of V_2O_5/TiO_2 is determined by vanadia–titania interactions, which are more evident for the V_2O_5/TiO_2 system prepared from liquid precursors.^{3,26}

In the case of the V_2O_5/TiO_2 catalytic system prepared by the impregnation method, all XRD spectra show the presence of both anatase and rutile phases, as are expected from the original structure of the titania support. Three very weak peaks of crystalline V_2O_5 are present in the spectra. Many authors^{15,27–29} reported the formation of monomeric vanadyl and polymeric vanadate species for vanadia loadings corresponding to less than the monolayer capacity of the TiO_2 support. Increasing the vanadia loading above the monolayer capacity of the TiO_2 support, crystallites of V_2O_5 are formed. For the P25 support, the monolayer capacity is estimated to be 4.0 wt % V_2O_5 ,¹⁴ but for our samples the monolayer capacity is higher.

B. Raman spectroscopy

Figure 2 displays Raman spectra of the catalysts showing a well-defined absorption band at 1030 cm^{-1} and two broad bands at $900\text{--}960$ and $770\text{--}850\text{ cm}^{-1}$. The band at 1030 cm^{-1} is attributed to monomeric vanadyls species bound directly to the TiO_2 support.^{30–34} The number of bonds anchoring the vanadyl group to the support cannot be determined from the Raman spectra. This assignment is based on the

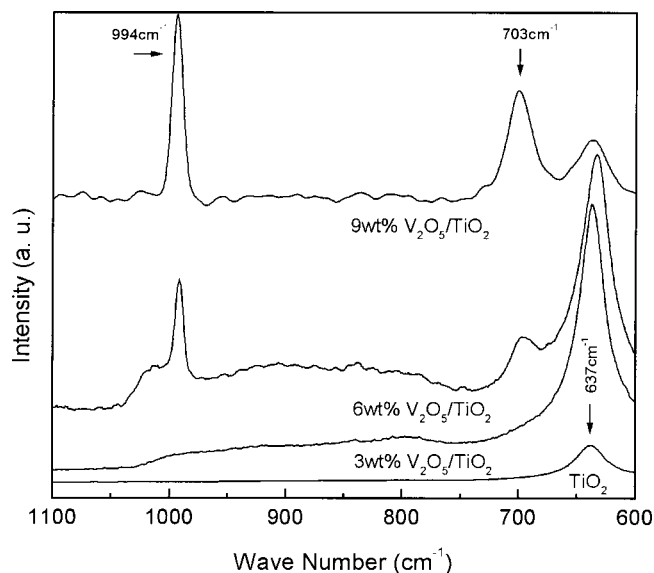


Fig. 3. Raman spectra of V_2O_5/TiO_2 prepared by the impregnation method dehydrated at 473 K under 10^{-3} Torr pressure.

similarity in the position of these bands and those for terminal $V=O$ bonds of polyvanadate anions in solution. As the number of vanadium centers in the polyvanadates increases, the number of terminal $V=O$ groups per vanadium decreases to accommodate $V-O-V$ linkages. The broad band in the region from 900 to 960 cm^{-1} , and centered at 930 cm^{-1} , is assigned to the terminal and internal $V=O$ stretches, $\nu(V=O)$, of polyvanadate groups, and the broad band centered at 822 cm^{-1} is attributed to the $\nu(V-O-V)$ vibration of polymeric vanadates.³⁴ Our Raman spectra do not exhibit the characteristic bands of crystalline V_2O_5 at 997 and 703 cm^{-1} .³⁴ These results are in agreement with those obtained by XRD and indicate an efficient dispersion of vanadium into the titania matrix.

According to comparative studies carried out by Vejux and Courtine⁴ using Fourier transform infrared spectroscopy and Raman scattering, the vibrational frequencies of vanadate species do not depend strongly on hydration/dehydration treatments.

The Raman spectra of samples prepared by the impregnation method are shown in Fig. 3. The 6 wt % V_2O_5 sample spectrum presents the bands of vanadyls and vanadates groups, but for the 9 wt % sample these bands disappear. The sharp and intense band at 998 cm^{-1} and the broad band at 703 cm^{-1} , corresponding to crystalline V_2O_5 , are clearly visible for both samples. The intensities of these two bands increase as the vanadia content increases from 6 to 9 wt %, indicating a decrease in the vanadium dispersion on the support surface. Contrary to the samples prepared by the sol–gel method, the increase in vanadium content in the samples prepared by impregnation causes a partial oxidation of V^{4+} to V^{5+} surface ions.

C. XPS analysis

The XPS binding energies of the main peaks are summarized in Table I. The O $1s$ satellite and the V $2p_{3/2}$ peaks

TABLE I. XPS characterization of the V_2O_5/TiO_2 samples.

V_2O_5 (wt %)	Binding energies (eV)			Surface atomic ratio (V/Ti)
	O 1s	Ti 2p _{3/2}	V 2p _{3/2}	
6 sol-gel	530.7 (78) 532.2 (22)	459.3	517.6	0.13
9 sol-gel	530.5 (88) 532.1 (12)	459.0	517.5	0.19
6 impregnation	530.7 (84) 532.0 (16)	459.4	517.1	0.18
9 impregnation	530.3 (79) 531.7 (21)	459.2	516.9	0.20

overlap, making it difficult to analyze the samples of low vanadia concentration (1 and 3 wt %). Two O 1s components, resolved by curve fitting, can be distinguished: (a) one between 530.3 and 530.7 eV and (b) the other between 531.7 and 532.2 eV. The number in parenthesis is the atomic percentage of each contribution to the O 1s peak. These binding energies refer to $Ti^{4+}-O$ and OH^- , respectively, in agreement with results obtained by Carley *et al.*³⁵ and Pouilleau *et al.*³⁶ The binding energy values for Ti 2p_{3/2} correspond to Ti^{4+} in an octahedral symmetry.³⁷ The presence of adsorbed hydroxyl species (OH) can be due to water adsorbed on the surface of the catalysts. The V 2p_{3/2} binding energy values are similar for all samples, corresponding to V^{5+} ions.²⁴ However, an overlap can occur for V^{5+} and V^{4+} peaks.

For the samples prepared by the impregnation method, the V/Ti ratios increase slightly as the percent of vanadium increases. In the case of the samples prepared by the sol-gel method, the V/Ti ratios increase with vanadium content on

the support is more pronounced, indicating an enhancement in the dispersion of the surface vanadium. The formation of crystalline V_2O_5 was not detected in the sol-gel samples by either XRD (Fig. 1) or Raman spectroscopy (Fig. 2). Thus, vanadium remained dispersed on the titania surface as monomeric vanadys groups and polymeric vanadates due to the high surface area, which is characteristic of the solids obtained by the sol-gel method.¹⁷⁻²³

D. EPR analysis

Figure 4 shows the Q-band EPR absorption derivative spectra of the 1 wt % V_2O_5/TiO_2 catalysts at 77 K. This EPR spectrum is well resolved and indicates the presence of at least three families of V^{4+} ions: two sets characterized by structured EPR signals (species A and B in Fig. 4) superimposed on a broad signal centered at $g \approx 1.93$ (signal C). Species A and B, which present a resolved hyperfine structure,

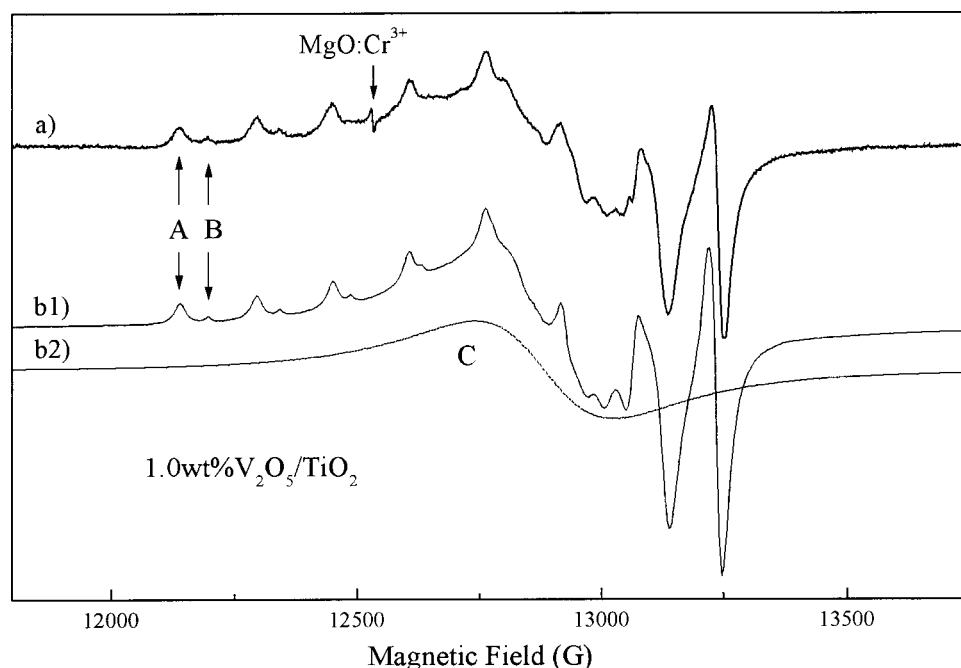


FIG. 4. EPR Q-band spectra of the 1 wt % V_2O_5 xerogel catalyst obtained at 77 K. The $MgO:Cr^{3+}$ ($g = 1.9797$) was used as a reference signal. (a) Experimental spectra and (b) Simulated spectra: (b1) hyperfine interactions and (b2) dipolar interactions.

TABLE II. Hamiltonian spin parameters for the V^{4+} ions obtained by computer simulation of the spectra.

Signal	g_{\parallel}	g_{\perp}	$A_{\parallel}(G)$	$A_{\perp}(G)$	$\Delta H_{pp}(G)$
A	1.956	1.901	152.37	39.25	12.5
B	1.953	1.905–1.910	141.30	25–39	7.1
C	1.926				200

are related to magnetically isolated vanadium ions. The broad and structureless signal C is due to magnetically interacting V^{4+} centers probably consisting of clusters or pairs of vanadium ions close enough to cause dipolar broadening of the EPR line and smearing the ^{51}V hyperfine structure. Similar spectra were previously observed for V_2O_5/TiO_2 catalysts for both the anatase and the rutile phases.^{1,3,22,25,38–41}

The experimental V^{4+} EPR spectra of the V_2O_5/TiO_2 catalysts were analyzed by numerically solving the Hamiltonian spin using Lorentzian line shapes. The best fittings of the experimental spectra were achieved for the Hamiltonian spin parameters summarized in Table II. As can be seen in Fig. 4, the simulated spectra closely reproduce the main features, including the position and the intensities of the prominent lines.

The analysis of the EPR parameters for signals A and B shows that species A differs from species B mainly in the value of the ^{51}V hyperfine constants (A_{\parallel} and A_{\perp}), which are definitely higher for species A. The fact that $g_{\parallel} > g_{\perp}$ and $A_{\parallel} > A_{\perp}$ for both species suggests that V^{4+} ions associated with signals A and B are located in sites with octahedral symmetry, substituting the Ti^{4+} in the titania matrix of the rutile structure.^{22,39–43} This may be due to the fact that the rutile phase of TiO_2 is tetragonal, with two nonequivalent Ti^{4+} ions per unit cell, where each ion is surrounded by six neighboring oxygen atoms, giving rise to an orthorhombic crystal field at the titanium ion position. Therefore, there are two nonequivalent Ti^{4+} ions whose positions can be occupied by substitutional V^{4+} ions.⁴¹

The spectra of the catalysts with lower loading (1–3 wt % V_2O_5 , not shown in this work) follow the general trends observed in Fig. 4. The EPR linewidths of the sample with the higher V_2O_5 concentration are significantly broader. This change in EPR line shape might be due to the interaction between V^{4+} ions resulting from increasing concentration of vanadia. The signals associated with the parallel components of the isolated vanadium (A and B) can be observed in all samples, but in the X band the distinction between these two signals is not as clear as in the Q band. Signal C, corresponding to vanadium pairs, which according to the literature^{1,3,22,25,38–41} can be located in the rutile or the anatase phase, giving rise to EPR lines with the same g factor.²⁷ A detailed analysis enables us to extract the linewidth of signal C as 200 G for the catalysts with lower loading and 250 G for the 9 wt % V_2O_5 catalysts.

This result is consistent with the interpretation given by XRD, Raman spectroscopy, and XPS for the catalysts obtained by the sol–gel and impregnation methods. XRD shows that the TiO_2 rutile structure (which contributes to the

A and B signals) decreases with the increase of vanadia. Raman spectroscopy, which probes the catalyst surface, shows that the vanadyl (V^{4+}) and vanadate (V^{5+}) groups are present in all samples prepared by sol–gel. The EPR intensities of signals A and B level off for higher vanadia content, and the intensity of signal C increases significantly. Thus, we conclude that a partial oxidation of V^{4+} to V^{5+} takes place for higher concentrations of V_2O_5 . The oxidation of V^{4+} in rutile has been reported in the literature.²²

IV. CONCLUSIONS

The sol–gel method employed for the preparation of V_2O_5/TiO_2 catalysts allows a better control of their composition, homogeneity, dispersion, and structural properties than the impregnation method. The increase of vanadium concentration induces the anatase formation. The formation of V_2O_5 crystallites was not observed in all samples. For the samples obtained by the impregnation method, the TiO_2 structure is independent of the vanadia loading, and crystalline V_2O_5 was observed. Raman spectra identified two species of surface vanadium: monomeric vanadyl and polymeric vanadates to xerogels and crystalline V_2O_5 in samples prepared by impregnation. XPS results indicated the presence of V^{5+} . The V/Ti atomic ratios showed that the sol–gel method favored the vanadium deposition on the titania surface, but some vanadium was incorporated into the rutile structure. At least three families of V^{4+} ions were identified: two isolated V^{4+} ions in locations with octahedral symmetry, substituting Ti^{4+} in the rutile structure, and magnetically interacting V^{4+} ions, present in pairs or clusters, giving rise to a broad and unresolved EPR line. For 9 wt % V_2O_5 , a partial oxidation of V^{4+} (paramagnetic) to V^{5+} (diamagnetic) was observed by EPR. The quantity of V^{4+} ions in the samples obtained by the impregnation method is very small.

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