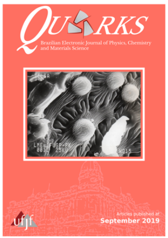
QUARKS: Brazilian Electronic Journal of Physics, Chemistry and Material Science
journal homepage: https://periodicos.ufjf.br/index.php/quarks
e-ISSN: 2674-9688



| Vol 1 | | No. 1 | | September 2019 |

Raman microscopy as a tool for the surface characterization of V_2O_5/TiO_2 catalysts before and after reaction with H_2O_2

Regina Celi Carvalho Costa[a] (reginacelicc@gmail.com), Flávia Maria de Sá Oliveira[a] (flaviasaoliveira@gmail.com), Adriana Paula Ferreira[b] (apf@ufscar.br) Luiz Fernando Cappa de Oliveira[a]* (luiz.oliveira@ufjf.edu.br)

[a] Núcleo de Espectroscopia e Estrutura Molecular (NEEM), Departamento de Química, Universidade Federal de Juiz de Fora (UFJF), Juiz de Fora, MG, 36036-900, Brazil.

[b] Departamento de Engenharia Química, Universidade Federal de São Carlos (UFSCar), São Carlos, SP, 13565-905, Brazil.

DOI: https://doi.org/10.34019/2674-9688.2019.v1.27911

Abstract

Supported vanadium oxides have been extensively used as catalysts in a variety of reactions, including selective oxidation of hydrocarbons, alkyl-aromatic and selective catalytic reduction of NO_x by NH_3. The high dispersion of vanadium in the form of a monolayer of VOx is the main reason for the better performance of the V_2O_5/TiO_2 system. In the present study we have examined the surface of supported V_2O_5/TiO_2 catalyst system by using Raman spectroscopy as well as the imaging technique obtained by Raman mapping; this technique is quite remarkable in following the relative intensity change of the band related to the V=O bond stretching, before and after reaction with H_2O_2. Raman mapping has been applied successfully to characterize single and mixed supported metal oxides and to investigate the structural changes of these metal oxides during reaction processes. The results have shown that V_2O_5/TiO_2 catalyst can promote the oxidation reaction of organic compounds, such as methylene blue, in aqueous medium and the reaction apparently takes place via active oxidizing species, such as V=O chemical group, which are generated in the vanadium surface.

Keywords: Heterogeneous catalysis; Raman mapping; Titanium oxide; Vanadium oxide.

---

*Corresponding author. E-mail: 🖃 luiz.oliveira@ufjf.edu.br

1. Introduction

Supported vanadium oxides have been extensively used as catalysts in a variety of reactions, including selective oxidation of hydrocarbons, alkyl-aromatic and selective catalytic reduction of NO_x by NH_3 [1-6]. A large number of works devoted to the oxidation reaction on vanadium oxides have also been published so far; many of these studies are concerned to the nature of vanadia species on oxide supports due to vanadium content, which has been identified as the key factor towards the activity [7]. Most catalysts based on vanadium oxide consist of a vanadium oxide phase deposited on the surface of an oxide support, such as SiO_2, Al_2O_3, TiO_2 or ZrO_2. Supporting a metal oxide on the surface of another oxide was initially proposed to improve the catalytic activity of the metal oxide phase due to a gain in the surface area and mechanical strength [8].

The reactivity of vanadium peroxides toward several different organic and inorganic substrates, such as thioethers, alkenes, alcohols, aromatic and aliphatic hydrocarbons is well known. These reactions, either stoichiometric or catalytic with the use of hydrogen peroxide or an alkylhydroperoxide as terminal oxidant, are generally carried out in mild conditions and are characterized by very high yields and selectivity. Upon addition of H_2O_2 to vanadium precursors several peroxo vanadates can also be produced in solution [10].

The presence of vanadium in magnetite is very common, where vanadium atom is frequently substituting the iron atom in the structure; there are relatively few studies about vanadium doped magnetites involving the effect of presence of vanadium on the physical–chemical properties of magnetite. However, those effects have not been sufficiently confirmed, which may greatly hinder the possible industrial applications of this material [11].

Vanadium oxide when supported on titania (TiO_2) is considered to be an effective catalyst system. The optimal activity and selectivity of the catalyst is accomplished when the vanadia is dispersed on the anatase phase of TiO_2 [12-13]. The catalytic performance of vanadium oxide, when supported on titanium oxide, compared to other supported oxides such as SiO_2 and Al_2O_3, is assigned to a strong and specific interaction between vanadium and the TiO_2. The high dispersion of vanadium in the form of a monolayer of VO_x is the main reason for the better performance of the V_2O_5/TiO_2 system. The similarity between the electronegativity of titanium and vanadium is the cause of the similar polarities of the titanium-oxygen and vanadium-oxygen bonds, and allows the vanadium oxide monolayer to act as an extension of the crystalline lattice of pure TiO_2 [14].

Since Raman spectroscopy technique can be used directly to obtain information about the surface of samples, it can be useful for the characterization of different vanadia species in several different supported systems, as for instance (i) $O{=}V(O)_3$; (ii) polyvanadate containing a single V=O bond, as well as V–O–V/V–O–M bonds (where M is the metallic cation of the support), and (iii) V_2O_5 crystallites [15]. Raman spectroscopy is also able to discriminate between different vanadium oxide coordination environments, due to the existence of different vanadium-oxygen bond distances and angles. Another practical importance for the use of Raman spectroscopy is that vanadium–oxygen vibrations are present around 1100 cm^{-1}, whereas the support oxides only show weak vibrational bands in the 700–1100 cm^{-1} region [16]. Raman can also be applied to study the structural changes during in situ conditions reactions, although it is not very sensitive to the reduced vanadium oxides (e.g. V^{4+} and V^{3+}) [12].

In the present study we have examined the surface of supported V_2O_5/TiO_2 catalyst system by using Raman spectroscopy as well as the imaging technique obtained by Raman mapping; this technique is quite remarkable in following the relative intensity change of the band related to the V=O bond stretching, before and after reaction with H_2O_2, in order to understand the relation between the catalytic cycle and the vibrational and structural properties of the catalyst surface [17-18].

2. Material and Methods

Catalyst preparation

The supported V_2O_5/TiO_2 catalysts were prepared by the impregnation method, where the support TiO_2 anatase (Aldrich 99.8 %) was added to an aqueous solution of ammonium metavanadate (NH_4VO_3); the suspension was stirred for 30 min at 700C followed by dryness for 12 hours at 1100°C. The material was calcinated in flowing oxygen at 450°C during 4 hours [12].

Experimental techniques

Raman spectra were collected on Lab Ram HR Horiba spectrometer; the 632.8 nm laser line was focused on the sample with a 10x objective, and no filter was used during measurements. The images were done in areas of 600X600 µm, in a spectral window in the range 950-1050 cm^{-1}, using diffraction grating of 1800 lines/mm, 2.0 seconds of exposure and one point for every 15 microns.

X-ray diffraction (XRD) patterns were recorded at room temperature on a Bruker–D4 Endeavor, using Co Kα (35 kV/40 mA), radiation scanning from 5 to 800 at scan rate of 1 second.

The catalytic activity of V_2O_5/TiO_2, in different vanadium concentrations, was tested against the discoloration of 3mL of a solution containing 0,01 g L^{-1} of methylene blue in the presence of H_2O_2 (0,32 mol L^{-1}). The color was monitored by spectrophotometer Shimadzu model UV1800, using quartz cuvettes of 10 mm. All the reactions were carried out using 30.0 mg of catalyst.

3. Results and Discussion

Catalyst characterization

The presence of the vanadia dispersed on the catalyst structure has been investigated by XRD, Figure 1a, before reaction with H_2O_2; the anatase phase is the predominant one, and it can be observed in all the investigated samples. It is also very clear that the $3V_2O_5/TiO_2$ sample shows isolated vanadium, which can be assigned to the presence of the V=O bond, very important to the catalyst activity (vanadium oxide, 1.6%). The XRD has also shown that the increase in the vanadium oxide concentration, lead to an increase of the crystalline phase (0.8% for $6V_2O_5/TiO_2$ and 1.5% for $9V_2O_5/TiO_2$); this implies in a decrease of the isolated form of vanadium oxide, which is not suitable for catalytic activity. After the reaction with H_2O_2, Figure 1b, the XRD data have not shown any differences, at least the ones seen by the technique; this result is expected since the structural changes which could happen in the surface are very small in quantity, once the vanadium oxide is present in very low concentration.

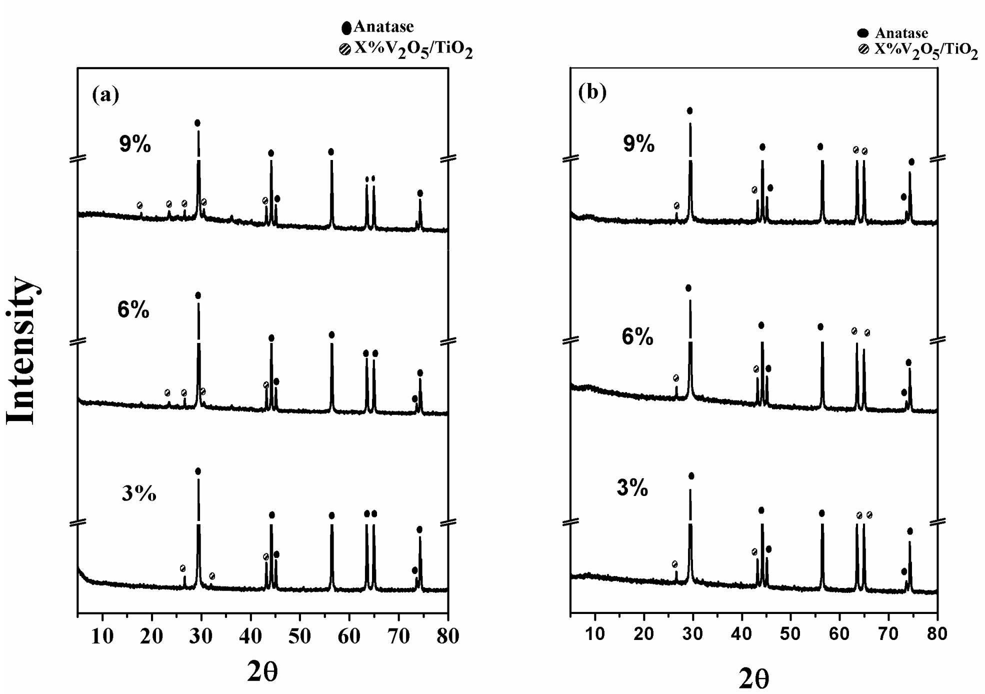


Figure 1. XRD diffractograms for TiO_2 supported in different concentration of X%V_2O_5/TiO_2 before (a), after (b) reaction with H_2O_2 (where X = 3, 6 or 9).

However, with the use of Raman spectroscopy it was possible to identify changes relating to the catalytic activity (Figures 2a and 2b), since Raman spectra can discriminate between different vanadium oxide coordination environments. Figure 2a shows the spectra of X%V_2O_5/TiO_2 before reaction with H_2O_2 (X represents the different vanadium oxide compositions), where the vanadium-oxygen stretching vibration [ν(V=O)] can be seen at 994 cm^{-1}. The Raman spectra show the presence of other bands at 144, 515 and 395 cm^{-1} corresponding to the anatase phase, whereas the band at 638cm-1 can be assigned to the bending of the V-O-Ti bonds [19]. However, it is straightforward to realize that the main vibrational band to the characterization is really the one at 994 cm^{-1}, which can be seen as a marker of all the changes performed on the catalyst surfaces during the reactions. It is also very important to notice that the lack of polymeric species such as metavanadate can be strongly suggested by the absence of a band in the region between 920 and 930 cm^{-1}.

After reaction with H_2O_2 the anatase phase is still predominant in the Raman spectra; however, the very important information is the absence of the band at 994 cm^{-1}, which is related to the decrease of the V=O bond vibrational mode, and consequently the decrease in concentration of the V=O species over the catalyst surface (Figure 2b). This diminution in the intensity of the V=O bond vibration is probably a consequence of the V^{5+} species reduction to V^{4+}/V^{3+} species in the catalyst surface, with the latter not being Raman active [20]. Based on these results, we can state that before and after the reaction with H_2O_2 the catalyst support remains the same, whereas the surface of the catalyst shows some changes which are not seen by XRD, but are seen by means of Raman spectroscopy, where the V=O bond stretching mode decreases in intensity because this chemical group is the one involved in the chemical reaction taking place on the surface of the catalyst.

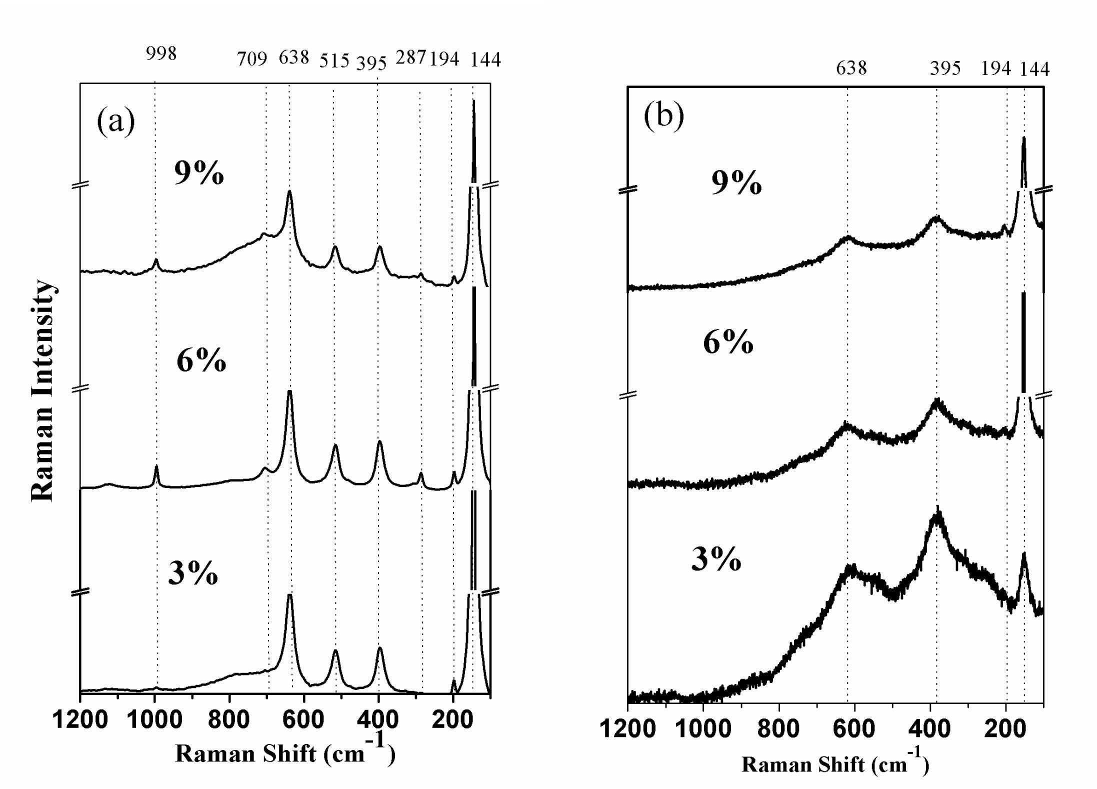


Figure 2. Raman spectra for TiO_2 supported in different concentrations of V_2O_5 (a) before and (b) after reaction with H_2O_2.

Raman spectroscopy combined with microscopy can provide molecular information with high spatial resolution; one of the potential uses of Raman microscopy is the obtaining of a Raman mapping, which is a method for generating detailed chemical images based on a Raman spectrum of a sample; these results can be presented as a spectroscopic map and can be directly compared to the corresponding visual image of the investigated surface sample. Other important achievement of Raman mapping is to provide detailed information regarding the distribution of the material in the surface, which is very important in catalysis in order to characterize the regions that are important for catalytic activity, as well as to monitor the active sites before and after the reaction on the catalyst surface.

In Figure 3 it can be seen all the Raman mapping of all the investigated materials; the Raman spectra were used to generate a surface mapping in order to analyze the presence of the stretching mode vibration of the V=O bond on the catalyst surface [21]. In Figure 3 the red color is related to the bigger intensity of the V = O band in surface of catalysts, whereas the green color is the opposite.

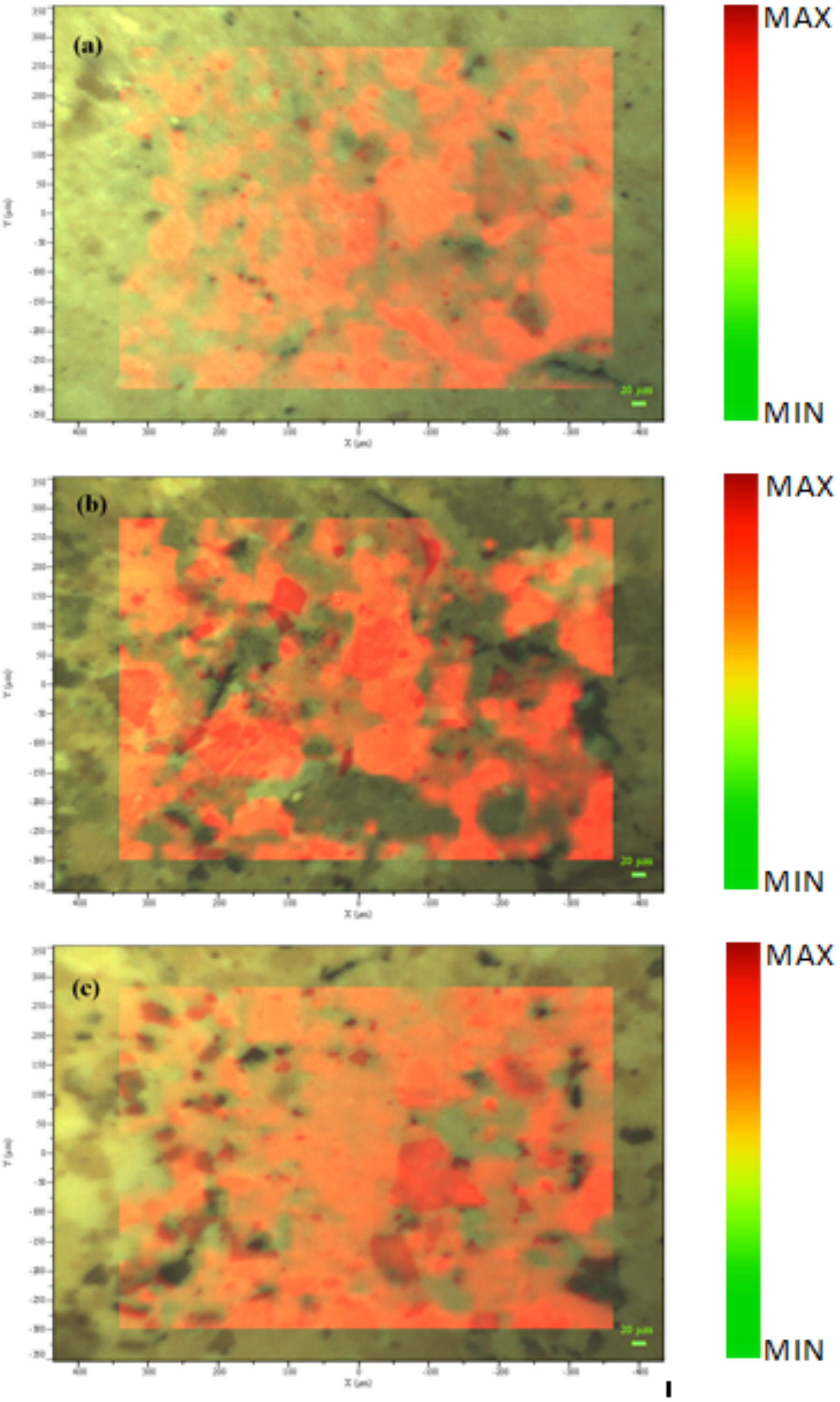


Figure 3. Image and Raman mapping obtained with 632.8nm laser excitation for samples with different concentrations of V_2O_5/TiO_2: (a) 3% of V_2O_5, (b) 6% of V_2O_5 and (c) 9% of V_2O_5.

The mapping shows vanadia is dispersed over the surface of TiO_2 catalyst and appears to be homogeneous, at least on the measurement limit of 15 microns. All Raman spectra provide one intense band near 1000 cm^{-1} assigned to the V=O bond stretching modes, and such bands can be used for the identification of the relevant regions associated to the catalytic activity. For this purpose single point Raman measurements and especially Raman mapping have been applied; the intensity of the red colors is related to the high concentration of vanadium oxide V=O bond, meaning that for the 3% sample there are more V=O bonds dispersed over the surface than the other samples (6 and 9%). In other words, the catalyst containing 3% of vanadium oxide dispersed on TiO_2 clearly shows a better dispersion and distribution of V=O bonds on the surface than the other prepared samples. It is important to observe that this same achievement was done by Dunn and coworkers, who have studied similar samples by means of ordinary Raman spectroscopy [22].

Figure 4 shows the mapping analysis by micro-Raman imaging after reaction with H_2O_2 for the same samples; clearly, it can be observed a decrease in the intensity of the V=O band on the catalyst surface after reaction with H_2O_2. Once again, the presence of the red color in the Raman mapping, related to the high intensity of the ν(V=O) band, is lower for the 3% sample when compared to the 6% concentration, thus corroborating the previous results for the reactions performed without H_2O_2.

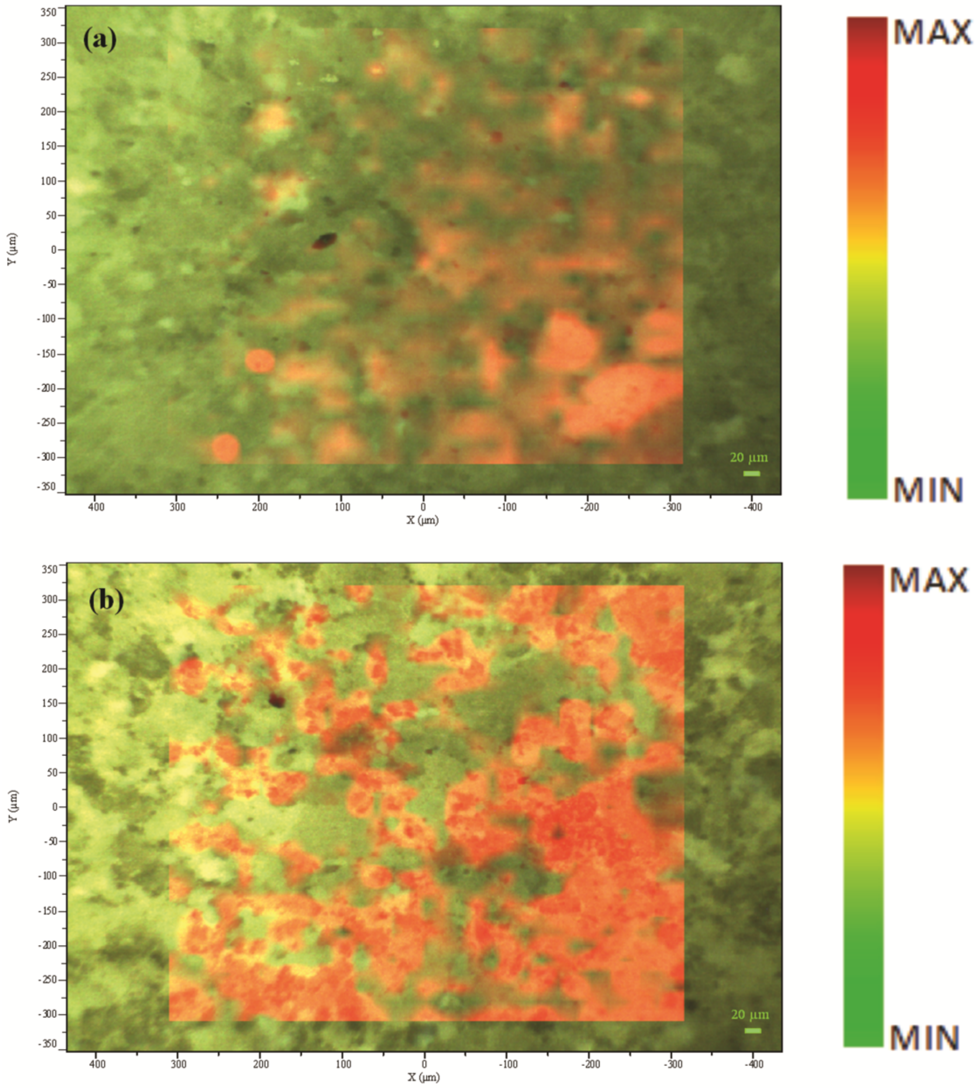


Figure 4. Raman mapping obtained with 632.8 nm laser excitation for samples with different concentrations of V_2O_5/TiO_2 after reaction with H_2O_2: (a) 3% of V_2O_5, (b) 6% of V_2O_5.

To evaluate the performance of the synthesized catalyst systems, the catalytic activity was tested using a very simple reaction between methylene blue dye and H_2O_2 as an oxidation agent, in the presence of the X%V_2O_5/TiO_2 system (where X = 3, 6 and 9%). Methylene blue dye is a very interesting probe molecule for oxidation reactions, since presents a high solubility in water and its oxidation can be monitored by simple spectrophotometric measurements. Figure 5 shows the discoloration plots obtained for the different catalytic samples, and the results have shown very high oxidation activities with up to 70% discoloration of the solutions during 10 minutes of reaction time. Once again, besides the three samples have shown a very good response for this type of reaction, the samples containing 3 and 6% of vanadium oxide displayed the best discoloration against methylene blue for a 1-hour time, whereas for 90 minutes the 3% sample has the best result.

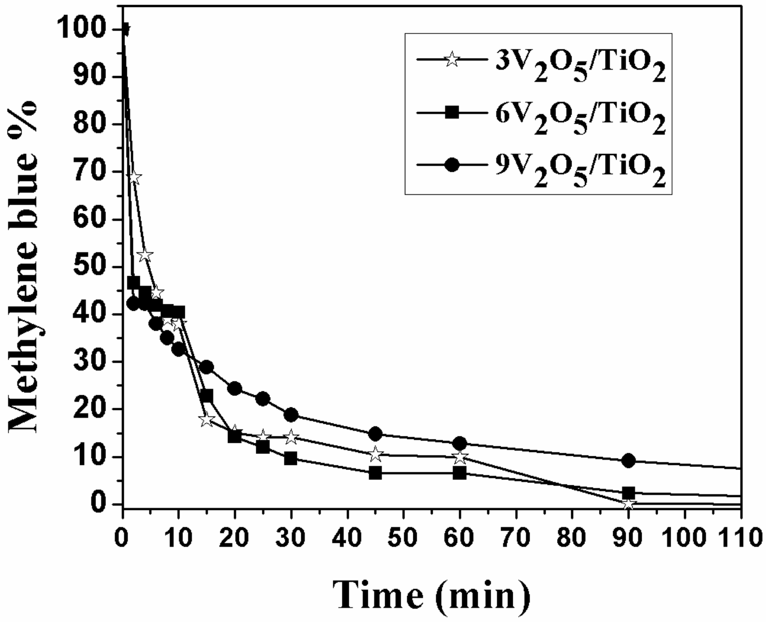


Figure 5. Discoloration of methylene blue in the presence of X% V_2O_5/TiO_2 and H_2O_2 (where X = 3, 6 or 9).

The decomposition of H_2O_2 promoted by transition metal oxides can lead to the formation of •OH or •OOH radicals, and such radical species are the ones responsible for oxidize all the organic molecules present in the reaction system [23]. Catalytic studies for several different oxidation reactions have demonstrated that the monomeric and polymeric surface VO_4 species are generally the catalytic active sites in supported vanadia catalysts, since the crystalline phases possess very few exposed active surface sites, and these sites are the ones responsible for the radical formation. It is important to notice that the VO_4 species present a V=O bond in the structure, which is the chemical group responsible for the activity reaction in the system; more than this, this chemical species is the one we are following by Raman mapping. Other important feature from our data is that the reaction apparently takes place via active oxidizing species which are probably generated by vanadium oxide dispersed over the surface. Summing up, the Raman mapping can show us the general view of the surface containing the most important chemicals involved in the reaction.

4. Conclusions

Raman spectroscopy, in special Raman mapping, has been applied successfully to characterize supported single and mixed titanium and vanadium oxides and to investigate the structural changes of these metal oxides during reaction processes.

Vibrational spectroscopy has proved to be of outstanding importance in heterogeneous catalysis research, and Raman imaging has proven to be a handy technique to monitor physical-chemical processes involved in the characterization of supported catalysts, in the preparation and also in monitoring reactions processes.

The present results have shown that V_2O_5/TiO_2 catalyst can promote the oxidation reaction of methylene blue in aqueous medium. The vibrational data strongly suggest the reaction takes place via active oxidizing species, such as V=O chemical group, which are generated by the vanadium surface.

Raman spectroscopy mapping seems to be a promising technique for the surface characterization of catalysts, since the image allows the characterization and monitoring of important chemical bonds of the catalyst during the reaction process.

Acknowledgments

Authors thank CNPq, FAPEMIG and FAPESP for financial support. They are also grateful to Prof. Rochel M. Lago, for synthesis facilities. This work is a collaboration research project of members of the Rede Mineira de Química (RQ-MG) supported by FAPEMIG.

References

[1] K.V. Narayana, A. Venugopal, K.S. Rama Rao, S. Khaja Masthan, V. Venkat Rao, P. Kanta Rao, *Appl. Catal*. A **1998**, 167, 11-22.

[2] C.R. Dias, M.F. Portela, G.C. Bond, *J. Catal*. **1995**, 157, 344-352.

[3] T. Mongkhonsi, L. Kershenbaun, Appl. Catal. A **1998**, 170, 33-48.

[4] A.A. Lemonidou, L. Nalbandian, I.A. Vasalsos, *Catalisys Today* **2000**, 61, 333-341.

[5] G. Centi, *Appl. Catal*. A **1996**, 147, 267-298.

[6] I. E. Wachs, Y. Chen, Jih-Mirn Jehng, L.E. Briand, T. Tanaka, *Catal. Today* **2003**, 78, 13–24.

[7] H. Tian, E. I. Ross, I. E. Wachs, *J. Phys. Chem*. B 2006, 110, 9593-9600.

[8] R. Neumann, M. Levin-Elad, *J. Catal*. **1997**, 166, 206-217.

[9] V. Conte, A. Coletti, B. Floris, G. Licini, C. Zonta, Coord. *Chem. Rev*. **2011**, 255, 2165-2177.

[10] X. Liana, S. Zhu, Y. Zhang, J. Zhu, P. Yuan, H. He, J. Zhang, *Appl. Catal*. B Environ.

2010, 97, 151-159.

[11] F. Cavani, C. Cortelli, A. Frattini, B. Panzacchi, V. Ravaglia, F. Trifiro, C. Fumagalli, R. Leanza, G. Mazzoni, *Catal. Today* **2006**, 118, 298-306.

[12] D.I. Enachea, E. Bordes-Richard, A. Ensuquea, F. Bozon-Verduraza, *Appl. Catal*. A Gen. **2004**, 278, 93-102.

[13] M.A. Bañares, *Catal. Today* **1999**, 51, 348-348.

[14] I.E.Wachs, C.A. Roberts, *Chem. Soc. Rev*. **2010**, 39, 5002-5017.

[15] B.M. Weckhuysen, D.E. Keller, *Catal. Today* **2003**, 78, 25-46.

[16] C. Resinia, T. Montanaria, G. Buscaa, J. Jehngb, I.E. Wachs, *Catal. Today* **2005**, 99, 105-114.

[17] T. Ono, H. Numata, *Journal of Molecular Catalysis A: Chemical* **1997**, 116, 421-429.

[18] E. Santacesaria, M. Cozzolino; M. Di Seri o, A.M. Venezia, R. Tesser, *Appl. Catal*. A Gen. **2004**, 270, 177-192.

[19] C. Zhao; I.E. Wachs, *Catal. Today* **2006**, 11, 332-343.

[20] E. Stavitski, B M. Weckhuysen, *Chem. Soc. Rev*. **2010**, 39, 4615-4625.

[21] R.C.C. Costa, F.C.C. Moura, J.D. Ardisson, J.D. Fabris; R.M. Lago, *Appl. Catal. B* Environ. **2008**, 83, 131-139.

[22] J.P. Dunn, J.M. Jehng, D. S. Kim, L. E. Briand, H. G. Stenger, I. E. Wachs, *J. Phys. Chem.* **102**, 1998, 102, 6212-6218.

[23] F. Magalhães, F.C.C. Moura, J.D. Ardisson, R.M. Lago, *Mat. Res*. **2008**, 11, 307-312.