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Spectroscopic surface characterization of MoVNbTe nanostructured catalysts for the partial oxidation of propane

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1. Introduction

A general trend in the design of catalytic materials nowadays is based on nanostructured catalysts, since they present valuable advantages from both industrial and academic points of view [1]. The active phases can be stabilized by a support versus syntherization on a non-expensive material that acts as support [2]. Thus, the amount of active phase required for a satisfactory catalytic performance, can be dismissed, and, in addition, the use of nano-scaled oxide phases maximizes the surface-to-volume ratio allowing a better insight on the nature of the active phase. Following this approach, in our group we have reported the synthesis and catalytic behavior of nanoscaled SbVO₄ [3] and VPO [4,5] based catalysts, and, recently, we have reported a very promising results with the use of nanoscaled MoVNb(Te)O catalysts for both propane oxidation [6] and amoxidation [7] reactions.

Since the understanding of the factors that determine the surface reactivity is necessary to design new and more effective catalytic processes; the aim of the present contribution is to analyze the effect of composition, coverage and tellurium doping on the surface composition and catalytic behavior of these novel nanoscaled

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ABSTRACT

The main objective of the present contribution is to analyze the effect of composition, coverage and Te doping in the surface composition and catalytic behavior of supported-nanoscaled MoVNb(Te)O catalysts. Different spectroscopy techniques combine to afford such objective. The composition of the surface species has been studied by Raman and UV–Vis spectroscopies, whereas it has been performed several pyridine adsorption experiments to quantify the number of acid sites on the surface of catalysts. The nature of reaction intermediates and the capability of the samples to adsorb them have been studied by FTIR spectroscopy combined with the adsorption of propene. The results have shown that tellurium induces several changes in the structure and catalytic properties of MoVNb catalytic materials, improving the reaction yield to the desired acrylic acid during the propane oxidation reaction.

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MoVNb(Te)O catalysts, by the use of different spectroscopic techniques, such as FTIR, UV–Vis and Raman spectroscopy. By this manner, it is possible to identify the surface species (by Raman and UV–Vis spectroscopies), the acid sites in each catalyst (determined from the FTIR spectra of pyridine adsorption) and the nature of reaction intermediates (determined form the FTIR spectra of propene adsorption), and all this information can be correlated with the catalytic test during the oxidation of propane into acrylic acid. The interest of this reaction is because acrylic acid is a useful intermediate that is currently obtained thought a two-steps process from propylene. Propane partial oxidation would replace the alkene as starting material, delivering acrylic acid in a single step, since actually the acrylic acid production is carried out in a two steps process, the first one is propylene to acrolein, and the subsequent transformation of acrolein to acrylic acid is the second one.

2. Experimental

The Mo–V–Nb–Te–oxide catalysts were prepared using the slurry method. An aqueous solution of ammonium heptamolybdate tetrahydrate (NH₄)₆Mo₇O₂₄·4H₂O (Sigma–Aldrich) was added to an aqueous solution of NH₄VO₃ (Sigma–Aldrich), heating and stirring at 80 °C for 50 min; then, an aqueous solution of ammonium niobium soluble complex (Niobium Products) and tellurium acid Te(OH)₆ (Sigma–Aldrich) was added using tartaric acid as



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complexing agent. This solution was kept under continuous stirring at 80 °C for 60 min until a wet gel was obtained; and then γ -Al₂O₃ support (Sasol Puralox SCCa-5/200) was added. The γ -Al₂O₃ support presented a BET surface area of 193 m²/g. The water excess was removed in a rotatory evaporator at 80 °C and in a reduced pressure of 10–40 mmHg. The resulting solid was dried at 120 °C for 24 h and then calcined at 600 °C for 2 h at a rate of 5 °C/min either in N₂ atmosphere. The catalysts were named as CMo₅V₄Nb_{0.5}(Te_{0.5}) with a final Mo/V/Te/Nb atomic ratio of 0.5–0.6/0.4–0.3/0.05–1/0.05; and they were prepared in order to have a total Mo+V+Nb+Te coverage (C) on alumina of 4, 8 or 12 atoms per nm² of support.

Specific surface areas were measured on a Micromeritics ASAP-2000 apparatus. Prior to the adsorption experiments, samples were outgassed at 140 °C for 2 h. Raman spectra were collected in a Renishaw System 1000 spectrometer equipped with green laser (Spectra Physics, $\lambda = 514$ nm, power 19 mW, 1 mW on sample) and a cooled CCD detector (-73 °C). The spectral resolution was ca. 3 cm⁻¹ and spectrum acquisition consisted of 10 accumulations of 30 s. The spectra were obtained under dehydrated conditions (ca. 200 °C) in a hot stage (Linkam TS-1500).

UV–Vis spectra were recorded on a Varian-Cary 300 Scan UV–Vis spectrophotometer with an integrated sphere CA-30I. Catalysts in the form of powders were placed into a cell equipped with a quartz window. The Kubelka–Munk function (F(R)) was used to convert reflectance measurements into equivalent absorption spectra using the reflectance of SPECTRALON as a reference.

Surface properties of the materials prepared were studied by in situ FT-IR spectroscopy of pyridine adsorbed. Self-supporting pellets of around 15 mg cm⁻² were prepared and located in a classical glass cell connected to a vacuum-adsorption apparatus for in situ experiments. IR spectra were recorded at room temperature with a Bruker Vector 22 FT-IR spectrometer (resolution 4 cm⁻¹). All the samples were activated in situ at 30 °C for 3 h under vacuum before adsorption of pyridine. Pyridine (Sigma–Aldrich) was adsorbed at 30 °C and evacuated five times at 30 °C for 30 min. After each evacuation the FTIR spectra were registered. The IR spectra of the activated samples were subtracted from those recorded after the adsorption of pyridine. The reported spectra are the results of this subtraction, and were used to calculate the number of acid sites of each type, with the equation [8–11]:

$$n_T = \frac{A_L C_d}{\varepsilon_L m} + \frac{A_B C_d}{\varepsilon_B m}$$

where:

 n_T = total number of micromoles of pyridine per gram of sample (g).

 A_L , A_B = integrated absorbance of FTIR bands due to base adsorbed at Lewis acid sites (L) or at Bronsted acid sites (B) (cm⁻¹). C_s = cross-sectional area of pressed disc (cm²). m = mass of the pressed disc (g).

 ε_L , ε_B = is the molar absorption coefficient for base at Lewis (*L*) sites or at Bronsted (*B*) sites (μ mol⁻¹ cm). ε_L = 1.5 μ mol⁻¹ cm; ε_B = 1.8 μ mol⁻¹ cm [12–15].

Propene adsorption and co-adsorption with oxygen were performed with the Vertex 70 (Bruker) spectrometer (resolution 4 cm^{-1}). The pressed wafers of the materials (around 15 mg cm^{-1}) were placed in the vacuum cell and activated at 30 °C for 3 h. The procedure was as follows: (i) propene adsorption at room temperature (RT) and heating at 50 °C for 30 min (ii) evacuation at RT for 60 min (iii) propene adsorption at RT followed by O₂ admission and heating at 50 °C for 30 min (iv) evacuation at RT for 30 min.

Activity measurements were performed using a conventional micro-reactor (9mm ID) with minimized void volume. The feed stream and effluents of the reactor were analyzed by an on-line gas-chromatograph equipped with flame ionization and thermalconductivity detectors. The accuracy of the analytical determinations was checked for each test by verification that the carbon balance (based on the propane converted) was within the cumulative mean error of the determinations ($\pm 10\%$). The catalytic tests were made using 0.2 g of powder sample with particle dimensions in the 0.25–0.125 mm range. The axial temperature profile was monitored by a thermocouple sliding inside a guartz tube inserted into the catalytic bed. Tests were made using the following reaction feed composition (% volume): 20.4% O₂, 12.5% propane and 15.9% steam in helium. The total flow rate was 40 ml/min, corresponding to $4800 h^{-1}$ gas hourly space velocity (GHSV). The quantity of catalyst and total flow were determined in order to avoid internal and external diffusion limitations. Yields and selectivities in products were determined on the basis of the moles of propane feed and products, considering the number of carbon atoms in each molecule.

3. Results and discussion

Fig. 1 shows the Raman spectra of all the catalysts obtained under dehydrated conditions. Just with a first view, it can be observed that there are some important differences in the shape of the spectra in Fig. 1A and B, suggesting that the differences in the surface structure of the catalysts without (Fig. 1A) and with (Fig. 1B) tellurium, even when a small amount of tellurium has been added. The spectra of the samples without tellurium are characterized by a broad signal near 800 cm⁻¹, related with the presence of a rutile structure and another broad signal near 1000 cm⁻¹ characteristic of the stretching modes of Mo=O and/or V=O bonds, respectively [16]. When both the total coverage as well as the molybdenum content is increased, the bands near 993 and 817 cm⁻¹ become sharper and more intense, and also appears a band near 285 cm⁻¹, the presence of this three bands indicate the presence of MoO_3 phase [6]. Thus, the presence of MoO_3 oxide is not detected when tellurium is present. Tellurium favors the presence of mixed oxides, thus, Fig. 1B shows a broad signal from 800 to 870 cm⁻¹, characteristics of rutile mixed phases. The spectrum of 12Mo₆V₃Nb_{0.5}Te_{0.5} presents in addition, signals near 870 and 885 cm⁻¹; that can be related with the presence of telluriumcontaining samples, the band near 870 cm⁻¹ can be assigned to the orthorhombic $Te_2M_{20}O_{57}$ phase (M=Mo, V, Nb), called M1 [17,18], whereas the signal near $880-890 \,\mathrm{cm}^{-1}$ can be assigned to the stretching mode of bridging Mo-O-M (M = Mo, V) bonds of highly distorted Te₂M₂₀O₅₇ on alumina [19].

Fig. 2 shows the UV–Vis DR spectra of the catalysts. A strong signal between 250 and 400 nm is assigned to ligand–metal charge transfer (LMCT) transitions involving primarily the charge transfer from oxygen ligands to Mo^{6+} or V^{5+} metal cations, in addition to Nb^{5+} and Te ⁴⁺ [20,21]. This band extends up to 600 nm when tellurium is added to the catalysts (Fig. 2B), suggesting the presence of reduced Mo cations [22–24]. The catalysts without tellurium with a high coverage (Fig. 2Ac and f) show a broad absorption at ~600 nm that is associated with V⁴⁺ cations [25–27].

Lewis acid (LAS) and BrØnsted acid centres (BAS) were detected in the FT-IR spectra after pyridine adsorption at 30 °C and desorption at the same temperature. According to literature, the interaction of pyridine with Lewis acid sites leads to the appearance of bands at ca. 1450 and ~1610 cm⁻¹ [28–31]. The intensity of the first one is related to the number of LAS, whereas the position of the second band characterizes the strength of LAS. Adsorption of pyridine on BrØnsted acid sites gives a band at ~1550 cm⁻¹ and two others in the 1620–1640 cm⁻¹ range. Moreover, the bands at 1445 and 1596 cm⁻¹, originate from pyridine hydrogen bonded to surface hydroxyls [29]. Figs. 3 and 4 show the FTIR spectra obtained



Fig. 1. In situ Raman spectra of dehydrated samples ($200 \degree C$ in 50 ml/min of air flow) of A: Te-free catalysts; (a) $4Mo_5V_4Nb_1$, (b) $8Mo_5V_4Nb_1$, (c) $12Mo_5V_4Nb_1$, (d) $4Mo_6V_3Nb_1$, (e) $8Mo_6V_3Nb_1$, (f) $12Mo_6V_3Nb_1$, and B: Te-containing catalysts; (a) $4Mo_5V_4Nb_{0.5}Te_{0.5}$, (b) $8Mo_5V_4Nb_{0.5}Te_{0.5}$, (c) $12Mo_5V_4Nb_{0.5}Te_{0.5}$, (d) $4Mo_6V_3Nb_{0.5}Te_{0.5}$, (e) $8Mo_6V_3Nb_{0.5}Te_{0.5}$, (f) $12Mo_6V_3Nb_{0.5}Te_{0.5}$, (g) $8Mo_6V_3Nb_{0.5}Te_{0.5}$, (h) $8Mo_5V_4Nb_{0.5}Te_{0.5}$, (h) $8Mo_5V$



Fig. 2. UV-Vis DRS spectrum of A: Te-free catalysts; (a) $4Mo_5V_4Nb_1$, (b) $8Mo_5V_4Nb_1$, (c) $12Mo_5V_4Nb_1$, (d) $4Mo_6V_3Nb_1$, (e) $8Mo_6V_3Nb_1$, (f) $12Mo_6V_3Nb_1$, and B: Te-containing catalysts; (a) $4Mo_5V_4Nb_{0.5}Te_{0.5}$, (b) $8Mo_5V_4Nb_{0.5}Te_{0.5}$, (c) $12Mo_5V_4Nb_{0.5}Te_{0.5}$, (d) $4Mo_6V_3Nb_{0.5}Te_{0.5}$, (e) $8Mo_6V_3Nb_{0.5}Te_{0.5}$, (f) $12Mo_6V_3Nb_{0.5}Te_{0.5}$.

after pyridine adsorption at 30 °C for catalysts with and without tellurium. The bands at 1615, 1490, and 1446 cm⁻¹ have been assigned to the vibrational modes of Lewis site coordinated pyridine. The bands at 1640, 1490 and 1538 cm⁻¹ correspond to a pyridinium ion bonded to a Brønsted site. Thus the band around 1490 is associated to both Brønsted and Lewis acid sites. The band at 1575 cm⁻¹ corresponds to physisorbed pyridine. Another band at 1595 cm⁻¹ is assigned to hydrogen-bounded pyridine (together with a shoulder at ~1437 cm⁻¹) [32]. This band seems to be more

pronounced for samples containing tellurium (Figs. 3B and 4B). The spectra of Tellurium containing catalysts exhibit noise characteristic for not fully evacuated water. It suggests that for these materials water is more strongly held and evacuation at room temperature, even 150 min, does not remove water totally. The significant difference in the spectra of catalysts with and without Tellurium one can find in the 1445–1450 cm⁻¹ range. Pyridine adsorbed on Te-containing samples gives rise to the formation of two IR bands originating from chemisorption on two different Lewis acid sites,



Fig. 3. IR spectra after pyridine adsorption at 30°C of A: Te-free catalyst (8Mo₅V₄Nb₁) and B: Te-containing catalyst (8Mo₅V₄Nb_{0.5}Te_{0.5}); (a) adsorption at 30°C, (b) desorption at 30°C, 30 min, (c) 60 min, (d) 90 min, (e) 120 min and (f) 150 min.



Fig. 4. IR spectra after pyridine adsorption at 30°C of A: Te-free catalysts (8Mo₆V₃Nb₁) and B: Te-containing catalysts (8Mo₆V₃Nb_{0.5}Te_{0.5}); (a) adsorption at 30°C, (b) desorption at 30°C, 30 min, (c) 60 min, (d) 90 min, (e) 120 min and (f) 150 min.

contrary to pyridine adsorbed on Te-free catalysts generating only one IR band in this range. This difference is especially well visible in Fig. 3. The detected presence of two different LAS centres on the surface of Te-containing catalysts can be caused by the presence of mixed phases identified by Raman (Fig. 1) and UV–Vis (Fig. 2) spectra.

Table 1 shows the relative acidity of the catalysts with and without tellurium, expressed as area under the peak at \sim 1445 cm⁻¹ normalized by surface unit in the spectra recorded after desorption at 30°C for 3 h. It can be observed that the acidity of the surface of the catalysts change upon tellurium incorporation. In the case of samples without tellurium, the major part of acid sites is Brønsted, and their number increases as the coverage is increased, since they are associated with the oxide phase [24]. The number of LAS decreases with coverage since the alumina sites are titrated when the coverage is increased. In the case of catalysts containing tellurium, the maximum number of acid sites is detected for intermediate coverage (8 atoms/nm²), although the presence of tellurium clearly decreases the number of acid sites. Thus, the changes in the structure of catalysts detected by both Raman and UV-Vis spectroscopies is also reflected in the changes detected in the surface acidity of the samples. The addition of Te induces the formation of mixed phases containing Te, such as M1, identified by Raman spectroscopy (Fig. 1), and also the presence of reduced Mo species identified by UV-Vis (Fig. 2), this changes in the structure inhibit the formation of MoO₃, since in the samples without Te this oxide has been identify by Raman spectroscopy (Fig. 1), and the number of acid sites when Te is present decreases. The formation of MoO₃ is also possible under reaction conditions, even when such oxide is not present in the fresh catalysts, and it has been demonstrated that the presence of Te in the catalyst formulation can inhibit the formation of such oxide under reaction conditions [33].

Fig. 5 shows the FTIR spectra obtained during the propene and oxygen adsorption experiments. After propene adsorption, the characteristic bands of propene adsorbed appear at 1439, 1368 (asymmetric and symmetric CH₃ deformations) and 1095 cm⁻¹ (isopropoxide species) on MoVNb(Te) [34]. These bands are visible after evacuation, indicative that propene remains retained on the surface of the catalyst. The admission of oxygen to these samples results in additional bands near 1440 cm⁻¹, characteristic of carboxylate compounds, and at 1298 cm⁻¹, assigned to acrylate type compounds [35,36].

Fig. 6 shows the subtracted FTIR spectra after propene adsorption and after admission of oxygen. Fig. 6A and C corresponds to the catalysts without tellurium, whereas Fig. 6B and D to the Te-containing samples. It is important to stress that the shape of spectra is totally different indicating that a small amount of tellurium is able to change the structure of the surface of the catalysts as well as the adsorption properties, and, subsequently, the catalytic properties. The bands are more intense in the case of catalysts without tellurium, which are those that presented a higher amount of acid sites. Thus, it confirms that the intermediates are held on the surface of catalysts strongly in the absence of Te, and such feature could decrease the activity of the samples. The band at 1631–1636 cm⁻¹ due to C=C stretching [37], together with other intense bands at 1452 and 1368 cm⁻¹, associated to the asymmetric and symmetric -CH₃ deformation are observed after propene adsorption at room temperature. When the oxygen is added, and specially in the case of the Te-containing samples, the intensity of the band at 1452 cm⁻¹ increases, together with an increase of intensity of the bands at 1456, 1465, 1368–1372 cm⁻¹. These bands can be assigned to a mixture of acetate ions and formate ions [34,38]. The 1441 and 1368–1386 cm⁻¹ IR bands correspond to the asymmetric and symmetric CH₃ deformations, while the band at 1095 cm⁻¹ is due to isopropoxide species [39]. The bands at 1440 and 1321 cm⁻¹ can be related also to carboxylic-type compounds

Table 1

BET surface area, compositions determined by ICP, and number of LAS and BAS sites.

Catalysts	Atomic ratio ICP	BET area (m²/g)	Number of $LAS^a \times 10^{18}$	$\begin{array}{l} Number \ of \\ BAS^a \times 10^{18} \end{array}$	Catalysts	Atomic ratio ICP	BET area (m²/g)	Number of $LAS^a \times 10^{18}$	$\begin{array}{l} Number \ of \\ BAS^a \times 10^{18} \end{array}$
4Mo ₅ V ₄ Nb _{0.5} Te _{0.5}	Mo _{5.5} V _{4.0} Nb _{0.29} Te _{0.21}	169	3.20	0.144	$4Mo_5V_4Nb_1$	Mo _{5.5} V _{4.0} Nb _{0.4}	172	4.28	6.05
8Mo ₅ V ₄ Nb _{0.5} Te _{0.5}	Mo _{5.0} V _{4.5} Nb _{0.23} Te _{0.27}	150	4.01	0.869	$8Mo_5V_4Nb_1$	Mo _{5.0} V _{4.5} Nb _{0.5}	157	2.22	10.5
12Mo ₅ V ₄ Nb _{0.5} Te _{0.5}	Mo _{5.4} V _{4.2} Nb _{0.20} Te _{0.30}	123	1.19	0.435	$12Mo_5V_4Nb_1$	Mo _{5.4} V _{4.2} Nb _{0.4}	128	1.84	11.9
4Mo ₆ V ₃ Nb _{0.5} Te _{0.5}	Mo _{6.4} V _{3.0} Nb _{0.30} Te _{0.20}	169	5.73	0.509	$4Mo_6V_3Nb_1$	Mo _{6.5} V _{3.1} Nb _{0.4}	170	3.99	6.39
8Mo ₆ V ₃ Nb _{0.5} Te _{0.5}	Mo _{6.5} V _{3.0} Nb _{0.25} Te _{0.25}	149	3.73	1.21	$8Mo_6V_3Nb_1$	Mo _{6.7} V _{3.0} Nb _{0.4}	153	2.01	9.18
12Mo ₆ V ₃ Nb _{0.5} Te _{0.5}	Mo _{6.5} V _{3.0} Nb _{0.21} Te _{0.29}	125	1.18	0.518	$12Mo_6V_3Nb_1$	Mo _{6.4} V _{3.2} Nb _{0.4}	132	1.96	9.39

^a Number of LAS (Lewis acid sites) and BAS (Brønsted acid sites) calculated in the catalysts on the basis of FTIR bands observed after desorption of pyridine expressed as area under the peak at ~1445 cm⁻¹ and ~1538 cm⁻¹, normalized by surface unit in the spectra recorded after desorption at 30 °C.



Fig. 5. FTIR spectra of C₃H₆ and O₂ coadsorption and desorption at room temperature and 50 °C, complete process.

[40]. Thus, this results show the capability of the samples to adsorb propene, which is the main intermediate during the propane partial oxidation [41]. The presence of IR bands characteristic for different oxygenates indicates that the catalysts are able to transform the adsorbed propene by inserting the oxygen atom into its molecule, in order to yield the desired acrylic acid; although it is not possible to make a definitive assignment of the intermediate adsorbed oxygenated compounds.

The catalytic results during the propane oxidation into acrylic acid are shown in Table 2. The yield to acrylic acid is higher in



Fig. 6. FTIR spectra after C_3H_6 adsorption and next O_2 admission in A: (a-b) $4Mo_6V_3Nb_1$, (c-d) $8Mo_6V_3Nb_1$, (e-f) $12 Mo_6V_3Nb_1$; B: (a-b) $4Mo_6V_3Nb_{0.5}Te_{0.5}$, (c-d) $8Mo_6V_3Nb_{0.5}Te_{0.5}$, (e-f) $12 Mo_6V_3Nb_{0.5}Te_{0.5}$; C: (a-b) $4Mo_5V_4Nb_1$, (c-d) $8Mo_5V_4Nb_1$, (e-f) $12 Mo_5V_4Nb_1$ and (D) (a-b) $4Mo_5V_4Nb_{0.5}Te_{0.5}$, (c-d) $8Mo_5V_4Nb_{0.5}Te_{0.5}$, (e-f) $12 Mo_5V_4Nb_{0.5}Te_{0.5}$.

Table 2

Propane conversion, selectivity to main products, and yield to acrylic acid obtained during the propane partial oxidation, reaction conditions: total flow 40 ml/min feed gas (vol.%) $C_3/O_2/H_2O/He = 12.5/20.4/15.9/51.2$, 200 mg, GHSV = 4800 h⁻¹, T = 400 °C.

Catalysts	Conversion	Acrylic Acid	Acrolein	Propylene	CO _x	Yield to acrylic acid
4Mo ₅ V ₄ Nb ₁	11.6	30.4	16.2	23.7	19.5	3.5
8Mo ₅ V ₄ Nb ₁	47.8	35.2	28.4	5.3	31.1	16.9
$12Mo_5V_4Nb_1$	31.8	22.8	11.8	9.3	54.2	7.3
4Mo ₆ V ₃ Nb ₁	3.14	30	25.4	30.9	5.7	1
8Mo ₆ V ₃ Nb ₁	10.5	48.6	17.7	22.3	3.8	5.1
$12Mo_6V_3Nb_1$	36.7	14.5	17.7	5.6	60.5	5.3
4Mo ₅ V ₄ Nb _{0.5} Te _{0.5}	27.5	37.0	20.4	30.7	11.3	10.1
8Mo ₅ V ₄ Nb _{0.5} Te _{0.5}	33.0	42.5	20.2	20.7	17.5	14.0
12Mo ₅ V ₄ Nb _{0.5} Te _{0.5}	51.0	44.7	9.5	12.4	31.5	22.7
4Mo ₆ V ₃ Nb _{0.5} Te _{0.5}	29.2	33.0	16.8	40.4	13.0	9.6
8Mo ₆ V ₃ Nb _{0.5} Te _{0.5}	32.0	44.3	17.9	25.8	11.6	14.2
$12Mo_6V_3Nb_{0.5}Te_{0.5}$	55.7	47.0	21.6	16.9	13.0	26.2

the case of Te-containing samples, especially those with higher coverages, and, in this case, the best results are reported for the catalysts with higher vanadium contents (8Mo₆V₃Nb_{0.5}Te_{0.5} and 12Mo₆V₃Nb_{0.5}Te_{0.5}), suggesting that vanadium sites are involved in the activation of the propane molecule. The catalysts without tellurium contain essentially fully oxidized molybdenum species and mixed phases with high oxidation states, although some oxygenates are detected in presence of propene and oxygen by FTIR (Fig. 6A and C), the acrylic acid yields obtained are guite low, due to a low propane conversion and a high selectivity to acrolein and CO_x .

4. Conclusions

The presence of different oxygenates molecules have been identified by FTIR spectroscopy on the catalysts surface under propene and oxygen atmosphere, indicative that these catalysts are able to transform the adsorbed propene by inserting the oxygen atom into its molecule, in order to yield the desired acrylic acid; although it is not possible to make a definitive assignment of the intermediate adsorbed oxygenated compounds.

The results of characterization (Raman and UV-Vis spectroscopies) have shown how the addition of tellurium to the catalysts formulation induces the formation of mixed phases containing Te, such as M1, identified by Raman spectroscopy and also the presence of reduced Mo species identified by UV-Vis, this changes in the structure inhibit the formation of MoO₃. In the absence of such oxidized compounds, the catalysts with Te present a lower surface acidity, as have been demonstrated with the pyridine adsorption experiments. The FTIR studies performed for the propene adsorption and oxygen admission indicated that the IR bands are more intense in the case of catalysts without Te, which are those that presented a higher amount of acid sites. It confirms that the intermediates are held on the surface of catalysts strongly in the absence of Te, and this behavior decrease the activity of the samples without Te.

Thus the combination of the application of different spectroscopies has led to the characterization of the surface species of catalysts used in this study and also has permitted to analyze the capability of the adsorption of the reaction intermediates. The strength of such adsorption can be related to the catalytic behavior.

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