Terpenes Functionalization: A Comparative Study in Catalytic Activity of Mesoporous Materials Modified with Ti and V

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Abstract: The catalytic performance of mesoporous materials with a MCM-41 structure in the reaction of α-pinene oxidation with H_2O_2 was investigated by a comparative study of Ti-MCM-41and V-MCM-41 catalysts. These materials were prepared by hydrothermal synthesis, from theoretical molar ratios silicon / metal (Si/M) = 20, 60 and 240 in the initial synthesis gel. The results of the catalytic evaluation showed that for a similar molar content of metal in the materials (0.023 mole of metal/100 g of catalyst), Ti-MCM-41 presented the best TON values. Moreover, V-MCM-41 showed a lower efficiency of H_2O_2 than Ti-MCM-41, which can be attributed to the presence of clusters species (V-O-V)$_n$ and nano-oxides V_xO_y which accelerate the decomposition reaction of peroxide to water. On the other hand, it is noteworthy that the polymerization degree of the surface vanadium species and the appearance of V_xO_y crystallites have a significant effect on the selectivity to the products obtained.

Keywords: Mesoporous materials, α-pinene, Oxidation, Ti-MCM-41, V-MCM-41.

INTRODUCTION

The homogeneous oxidation reactions in the liquid phase generally employ soluble metal salts or complexes in combination with different oxidants. However, the use of these catalysts has the disadvantage that its active species tend to dimerize/oligomerize to less reactive oxo species [1]. Thus, isolating the active species on solid inorganic matrices is a very effective way to resolve this problem. Various strategies can be employed for immobilizing active elements in a solid (inorganic) matrix [2]. Metal ions can be isomorphously substituted in framework positions of molecular sieves via hydrothermal synthesis or post synthesis modification such as impregnation and ion exchange [1-3]. It is known that the use of hydrothermal synthesis results in greater incorporation of the active species than using the impregnation technique [4]. Particularly, the M41S family of mesoporous materials has acquired great importance due to the possibility of adapting their catalytic properties such as type and force of acid and/or basic sites, hydrophilicity/hydrophobicity, structure and size of pores [5]. Since 90s the trend has been to modify MCM-41 structures with several transitional metals such as Ti, V or Nb with the aim to prepare catalyst with redox properties, to be applied in fine chemistry reaction [6, 7]. Thus, Ti-MCM-41 and V-MCM-41, are widely studied because of their potential catalytic

properties in the olefin and alcohol selective oxidations. Parvulescu *et al.* reported the oxidation of different hydrocarbons such as styrene, benzene, cyclohexanol with H_2O_2 under mild conditions using MCM-41 catalyst modified with V [8]. Shylesh et al. studied the cyclooctene oxidation obtaining conversions above 30% with molar ratio Si/V: 25 and substrate/ H_2O_2: 4/1 after 12 h of reaction [9]. Meanwhile, the organic compounds oxidation and especially olefinic compounds over Ti-based catalysts using H_2O_2 as oxidizing agent, have gained considerable interest [2, 10-12]. Among the functionalization reactions of cyclic olefins, the terpenes oxidation is of industrial importance due to the possibility of transforming cheap and readily available substrate, such as α-pinene, to valuable intermediates for chemical synthesis. Furthermore, oxygenated derivatives are used as the starting product for the synthesis of fragrances, flavours and therapeutics agent. The α-pinene gives valuable oxygenated products, such as campholenic aldehyde (2), verbenol (5) and verbenone (6) (Fig. **1**). The campholenic aldehyde is an important intermediate for the synthesis of santalol, the main constituent of natural sandalwood oil [13-15], while verbenol and verbenone are used as intermediate for the pesticides manufacture and the flavoring industry [16-18]. Among the oxidation products of α-pinene, verbenone is of great interest as it can provide a possible starting point for the synthesis of taxol, an important therapeutic agent [13, 19-21].

In this work, the catalytic performance of mesoporous materials with a MCM-41 structure in the reaction of α-pinene oxidation with H_2O_2 was investigated by a comparative study of Ti-MCM-41and V-MCM-41 catalysts, prepared by hydrothermal synthesis [22, 23]. Special attention was

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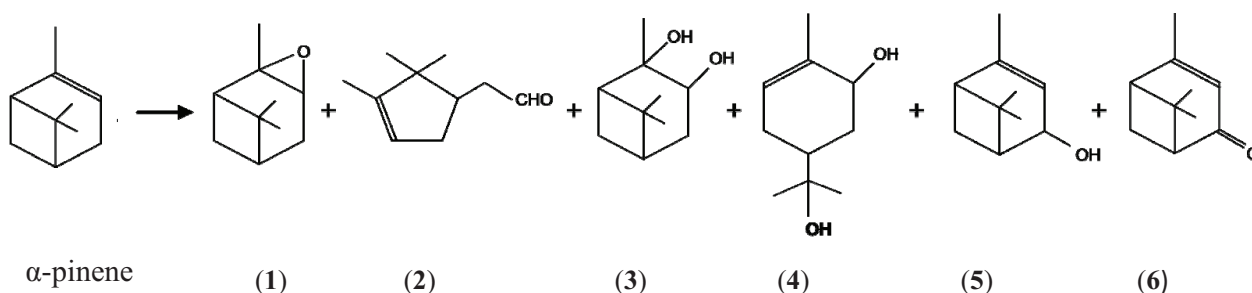
Fig. (1). Products obtained from α-pinene oxidation. α-Pinene oxide (**1**), campholenic aldehyde (**2**), 1,2 pinanediol (**3**), trans-sobrerol (**4**), verbenol (**5**), verbenone (**6**).

Table 1. Chemical Composition of MCM-41 Modified with Ti and V.

Metal Content (wt. %)[a]	Si/M[b]		
	240	60	20
Ti	0.240	1.120	2.500
V	0.035	0.140	1.210

[a] In the final solid
[b] Molar ratio in the initial synthesis gel

paid on the correlation between the structural properties of the materials obtained with their catalytic activity.

MATERIALS AND METHODS

Catalyst Synthesis and Characterization Techniques

Ti-MCM-41 and V-MCM-41 evaluated in this work were prepared by hydrothermal synthesis using cetyltrimethyl ammonium bromide (CTABr) as template and tetraethoxysilane (TEOS) as Si source and Ti (IV) isopropoxide (Fluka, 98%) and $VO(SO_4).H_2O$ (Aldrich, 99,99%) as Ti and V source respectively [22, 23]. The pH of the synthesis was adjusted to 13 by adding of a tetra ethyl ammonium hydroxide (TEAOH) 20 wt% aqueous solutions. Precursors were mixed and maintained under stirring during 3 h; afterwards the resulting gel was heated at 100 ºC in a Teflon-lined autoclave under autogenic pressure for a given time [23, 24]. The catalysts were synthesized from molar ratios of silicon/metal (Si/M): 20, 60, and 240. The solid obtained was filtered, washed with distilled water and dried overnight at 60 ºC. The template agent was evacuated from the samples by heating (2 ºC/min) under N_2 flow (45 mL/min) at 773 K for 6 h and subsequent calcination at 500 ºC for 6 h under dry air flow (45 mL/min).

The characterization of the materials evaluated in this work was previously reported [22-24]. Here, we mention only those aspects which are most relevant to compare the materials studied.

α-Pinene Oxidation

The chemical reactions were carried out in a glass reactor with a magnetic stirrer, immersed in a thermally controlled bath at 70 ºC. Typically, the reaction mixture consisted of 6.14 mmol of α-pinene, 1.54 mmol of H_2O_2 35%, 92.19 mmol of acetonitrile and 54 mg of catalyst. Reaction pro-

gress was followed taking samples during reaction through sealed septa by means of a syringe. Liquid samples were filtered and analyzed by gas chromatography using a capillary column (crosslinked methyl–silicone gum) connected to a FID detector. Reaction products were identified by mass spectrometry in a Shimadzu GCMS-QP 5050 with HP-5 capillary column. The α-pinene conversion was defined as the ratio of converted species to initial concentration and the selectivity as (mol product/mol total products) x 100. The turnover number (TON) was defined as moles of olefin converted/mol of metal in the catalyst. Finally, the total conversion of H_2O_2 was measured by iodometric titration and H_2O_2 efficiency was calculated as the percentage of this reactive converted to total oxidized products.

RESULTS AND DISCUSSION

Table **1** summarizes the chemical composition of mesoporous materials modified with Ti and V selected for this study. The metal content in each catalyst was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) after the digestion of the samples. As it can be seen, although the molar ratios of silicon/metal (Si/M) used in the initial synthesis gel for both metals were the same, the content of Ti in the final solid was considerably higher than the content of V for the three relationships studied. The reason why the material incorporates different amounts of metal, remains unclear. A possible explanation to understand this behavior could be considering the different hydrolysis reaction rate for each metal precursor, taking into account also the nature of the sources used, (alkoxide of the Ti and inorganic salt of V) [25, 26]. Hence, many kinds of metals can be hydrolyzed with ease and be transformed to metal oxide via a condensation-polymerization reaction. It is known that the reaction rates of hydrolysis of transition metals depend on the electron affinities, sizes, charges and coordination numbers of metal ions [27-29].
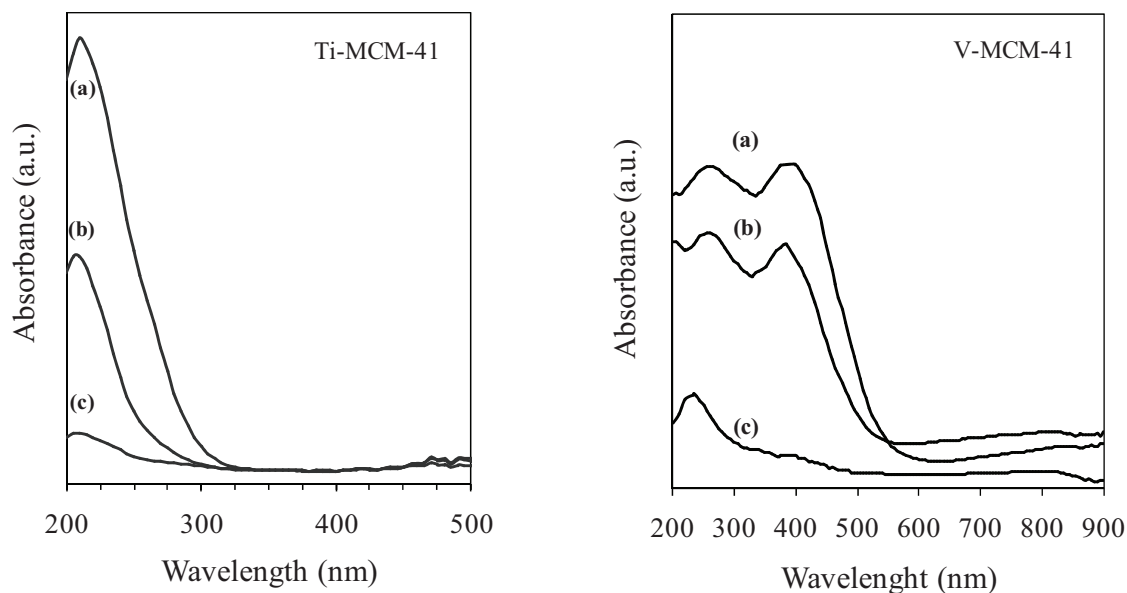
Fig. (2). UV–vis diffuse reflectance spectra of the calcined Ti-MCM-41 and V-MCM-41 catalysts. Si/M: (**a**) 20, (**b**) 60, (**c**) 240.
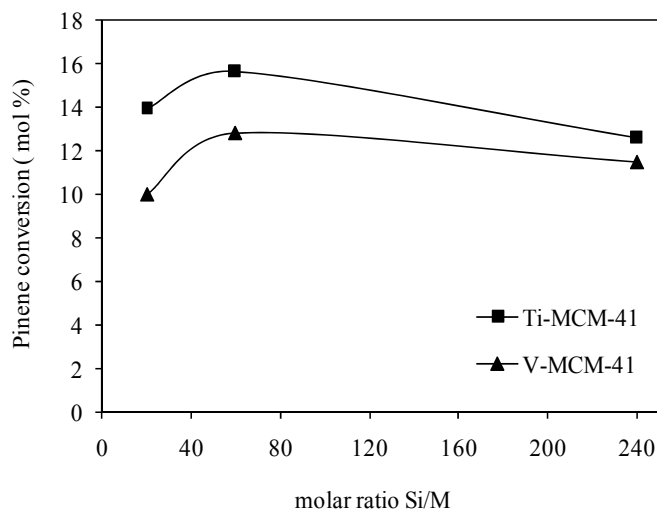

Fig. (3). α-Pinene conversion for reaction with Ti-MCM-41 and V-MCM-41. Reaction conditions: molar ratio substrate/oxidant: 4/1, temperature: 70 °C, catalyst: 9 mg/mL, reaction time 7h.

The Diffuse reflectance UV-visible (UV-Vis-DR) spectra of Ti-MCM-41 samples (Fig. **2**) showed an intense band at 210 nm in all the samples indicating that most of the Ti species are isolated and in tetrahedral coordination inside the framework. Moreover, the intensity of the 210 nm band is substantially increased and the position of the maximum does not shift towards higher wavelengths with increasing Ti content. Such behavior suggests that the tetrahedral component of Ti (IV) prevails even in the samples synthesized with high Ti content. A shoulder at 250–270 nm becomes significant in the samples with relatively high Ti content, which can be attributed to the presence of some $(Ti–O–Ti)_n$ clusters in the framework due to an incipient oligomerization of Ti species [21-22]. Furthermore, the presence of higher coordination Ti species probably due to the insertion of water molecules upon hydration cannot be unequivocally excluded [22].

The absorption band around 260 nm in the spectra for the sieve modified with V indicates that of V ions are isolated and in tetrahedral coordination possibly with the lattice oxygen (Fig. **2**). A second band at 370 nm, which is in the samples Si/V= 60 and 20, can be attributed to the presence of some $(V–O–V)_n$ clusters due to an incipient oligomerization of V species and/or to a higher coordination of V ions [23]. Finally, a new band around 450 nm only appears for the higher V content catalyst. This band could be attributed to V ions in the octahedral symmetry in V_xO_y crystallites. These nano-oxides can possibly be generated as consequence of a further polymerization degree of the V species due to the high content of V in the initial synthesis gel.

Ti-MCM-41 and V-MCM-41 catalysts were tested in the reaction of α-pinene oxidation with H_2O_2 at 70ºC. Fig. (**3**) shows the effect of the molar ratio variation Si/M in the initial synthesis gel on the oxidation of α-pinene. The general
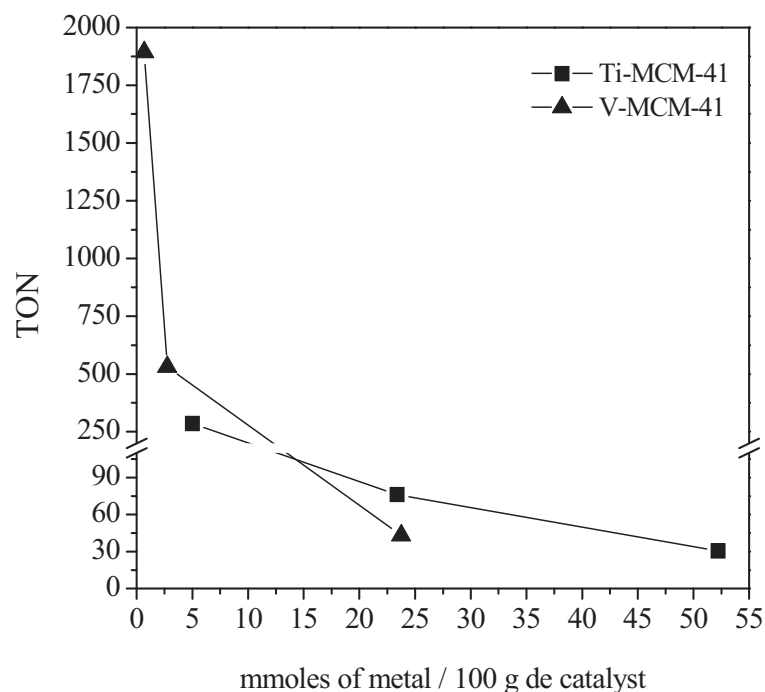
Fig. (4). TON values as a function of the metal moles in the final solid. Reaction conditions: molar ratio substrate/oxidant: 4/1, temperature: 70 °C, catalyst: 9 mg/mL, reaction time7h.

Table 2. Conversion and Efficiency of H_2O_2

Si/M	wt. %	Metal Molar Loading*	H_2O_2 Conversion (mol %)	H_2O_2 Efficiency (mol %)
Ti	1.120	0.023	81.46	75.66
V	1.210	0.023	91.26	38.34

*moles metal/100 g catalyst

trend is that Ti-modified materials showed a slightly higher activity than that of V; however, this increase was not the expected considering the total amount of metal in the final solid. Besides, as it can be seen, for the metal content increasing, (Si/M 240 to 60), the α-pinene conversion increased for both materials. These results could be interpreted taking into account the higher proportion of isolated Ti and V ions in tetrahedral coordination in the samples of molar ratio 240 and 60, which would be the active species in the α-pinene oxidation [12, 23]. Meanwhile, for materials with high metal loading, Si/M = 20, the lowest activity can be associated to the incipient oligomerization of Ti species forming small clusters. In the case of V this behavior can be related to an incipient oligomerization of V species and the V_xO_y nano particles observed, as it was already mentioned, by UV-Vis-DR. These nanoparticles could be located inside the material channels, as well as on the external surface, thus diminishing or blocking the accessibility to the active sites (isolated V ions), which causes a decrease of the catalytic activity [22, 23].

On the other hand, according to literature, the intrinsic catalytic activity of different catalysts can better be compared using the turnover number (TON), defined as moles

converted per active site [30]. Thus, in the Fig. (**4**) TON values are presented for the materials Ti and V with respect to the metal molar loading, which is defined as moles of metal/100 g of catalyst. In this way, for a content of 0.023 moles of metal (Ti or V)/100 g of catalyst, the material modified with Ti showed better catalytic performance. The activity differences of the two catalysts could be attributed to the redox nature of the two 3d transition metals (Ti and V), since it is known that the lower the density of the outer d-electron, the stronger the capacity to activate the H_2O_2 as was observed in the Ti-MCM-41 [31].

Moreover, to complete the analysis we must consider the parallel reaction of decomposition of peroxide to water. Table **2** lists the H_2O_2 conversion data for Ti-MCM-41 and V-MCM-41 with the same metal molar loading. Thus, taking into account that the distribution of metallic species determined by UV-vis-DR are different for Ti and V-MCM-41, the lowest efficiency of H_2O_2 observed with the mesoporous material modified with V probably derives from the formation of highly coordinated vanadium species. These species, present as clusters and nano oxides, would be responsible for the parallel reaction of peroxide decomposition in water decreasing the efficiency.
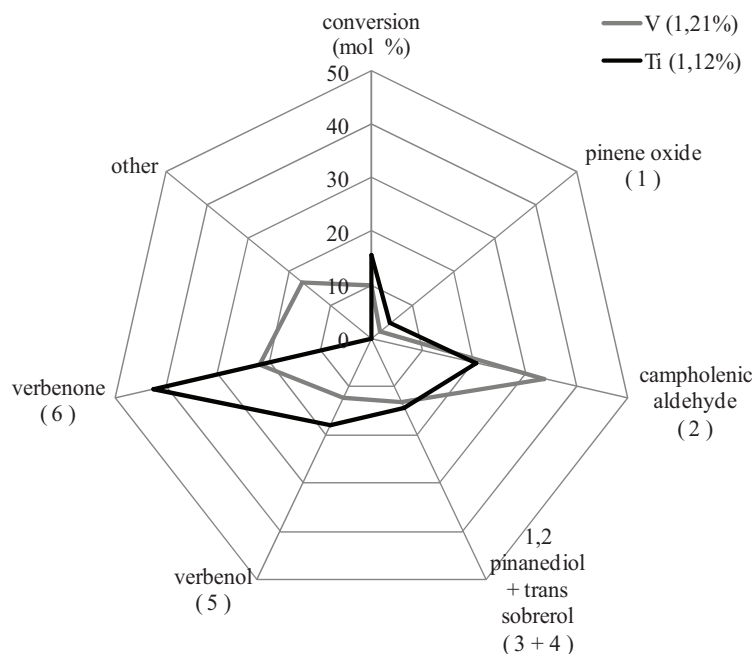
Fig. (5). Products selectivity for the α-pinene oxidation over Ti-MCM-41 (1.120%) and V-MCM-41 (1.210%).

Finally, Fig. (**5**) shows the different products observed for 7 h reaction for Ti-MCM-41 and V-MCM-41 catalysts. According to GC–MS analyses, the products mixture is composed of species formed by oxidation of both double bond (**1**, **2**, **3** and **4**) and allylic C–H bond (**5** and **6**), being verbenone and campholenic aldehyde the major products for the Ti-MCM-41 and V-MCM-41 respectively. Furthermore, with V-MCM-41 were obtained over-oxidation products which were named as other. This behavior would be giving account that the vanadium surface density is a quite important parameter that affects the selectivity of the reaction of α-pinene oxidation. Thus, the polymerization degree of the surface vanadium species and the appearance of V_xO_y crystallites have a significant effect on the selectivity to the products obtained. Probably, the α-pinene may react over two V atoms of $(V-O-V)_n$ species favoring the consecutive reactions of over-oxidation and decreasing the selectivity to interest products [32].

CONCLUSIONS

Mesoporous materials modified with Ti and V were synthesized from theoretical molar ratios Si/M: 20, 60 and 240 in the starting gel, yielding greater incorporation of metal for the Ti series. All tested materials were active in the α-pinene functionalization with H_2O_2. The intrinsic catalytic activity of the synthesized catalysts was compared using the turnover number (TON) with respect to the metal molar loading. Thus, for a content of 1.120 wt. % Ti and 1.210 wt. % V that is 0.023 mole of metal (Ti or V)/100 g of catalyst, a better performance of catalytic activity was achieved on the Ti modified material.

On the other hand, the V catalyst showed a lower H_2O_2 efficiency, which could be attributed to the formation of highly coordinated vanadium species, present as clusters and nano oxides determined by UV-Vis-RD. Thus, the presence

of these species could accelerate the decomposition reaction of peroxide to water reducing its catalytic performance**.**

Regarding the distribution of products verbenone and campholenic aldehyde were obtained as the major products for the Ti-MCM-41 and V-MCM-41 respectively. Furthermore, with V-MCM-41 were obtained over-oxidation products. This behavior would give account that the polymerization degree of the surface vanadium species and the appearance of V_xO_y crystallites could promote the consecutive reactions of over-oxidation and decreasing the selectivity to interest products.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

ACKNOWLEDGEMENTS

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