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Selective oxidation of C_3–C_4 olefins over Mo-containing catalysts with tetragonal tungsten bronze structure

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ABSTRACT

Mo–V–Nb–P–O-based catalysts with a tetragonal tungsten bronze-type (TTB) structure have been prepared hydrothermally from a $H_3PMo_{12}O_{40}$ Keggin-type heteropolyacid. These catalysts have been tested in the oxidation of C_3–C_4 olefins (propene, isobutene and 1-butene). Although the catalytic performance depends on the nature of the olefin fed the TTB-type catalysts prepared in the presence of elements of the V and VI groups such as Te, Sb and Bi have shown a high selectivity to partial oxidation products, especially that with Te. However, in the absence of these elements the TTB-catalysts present a high catalytic activity to deep oxidation. The selectivity to partial oxidation products decreases in the order: MoVNbPTe- > MoVNbPSb- > MoVNbPBi- > MoVNbP-TTB catalysts. The reaction products obtained in the oxidation of each olefin will be discussed according to their corresponding reaction mechanism and the characteristics of catalysts.

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1. Introduction

The increasing importance of selective oxidation process to synthesize valuable compounds has led to many research groups to intensify their work in order to develop more efficient catalysts that achieve high activity and selectivity. The discovery of MoVTe(Sb)NbO catalysts has meant a new impulse in the field of selective oxidation of hydrocarbons. MoVTe(Sb)NbO oxidic bronze catalysts, firstly reported by Mitsubishi [1,2], have shown a high efficiency in several reactions: (amm)oxidation of propane [3–6], oxidative dehydrogenation of ethane [7,8], or *n*-butane [9].

The two major phases in this mixed oxide catalyst, the so-called M1 ($Te_2M_{20}O_{57}$) and M2 ($Te_{0.33}MO_{3.33}$) (M=Mo, V, Nb), have been proposed to be responsible for high partial oxidation of alkanes [10–13]: M1 phase related to the activation of alkanes and olefins and M2 (which is only active in olefin partial oxidation) related to the high selectivity to oxygenated products. However, the catalytic performance of these catalysts strongly depends on the catalyst preparation procedure. It has been suggested [12] that orthorhombic M1 phase as well as trigonal Mo_3VO_x [14], are formed through a self-organization of Anderson type polyoxometalates. So, the starting materials used in the preparation of these materials have a remarkable importance in the formation of the desired crystalline phases.

It has been recently reported that MoVNbO mixed metal oxides with a tetragonal tungsten bronze (TTB) structure can be prepared hydrothermally from Keggin-type heteropolyacids, probably also as a self-organization of the corresponding Keggin-type hetero-polyoxometalate [15]. These materials are active and selective in the propylene oxidation to acrolein and/or acrylic acid depending on the catalyst composition.

In the present work, it will be shown that the catalytic performance of these TTB-MoVNbP catalysts in the oxidation of short chain olefins (propylene, isobutylene and 1-butylene) are completely modified when trivalent and tetravalent elements of the V and VI groups (Sb, Bi and Te) are present in the hydrothermal process and then incorporated to the framework of TTB structure. The role of each element in the catalytic performance of these catalysts is also discussed.

2. Experimental

2.1. Catalyst preparation

The catalysts have been prepared hydrothermally from gels containing $H_3PMo_{12}O_{40}$ (Aldrich), vanadyl sulphate (Aldrich),

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Table 1
Chemical composition of TTB bronzes determined by EDX analysis

	Catalyst			
	TB-O	TB-Sb	TB-Bi	TB-Te
Global composition	$MoV_{0.21}Nb_{0.45}\ P_{0.05}$	$MoV_{0.12}Nb_{0.21}P_{0.05}Sb_{0.19}$	$MoV_{0.17}Nb_{0.32}P_{0.05}Bi_{0.05}$	$MoV_{0.20}Nb_{0.40}P_{0.05}Te_{0.11}$
Particle 1	$MoV_{0.15}Nb_{0.46}\ P_{0.04}$	$MoV_{0.14}Nb_{0.31}P_{0.06}Sb_{0.07}$	$MoV_{0.11}Nb_{0.18}P_{0.07}Bi_{0.03}$	$MoV_{0.19}Nb_{0.39}P_{0.03}Te_{0.09}$
Particle 2	$MoV_{0.17}Nb_{0.43}\ P_{0.04}$	$MoV_{0.16}Nb_{0.40}P_{0.07}Sb_{0.07}$	$MoV_{0.12}Nb_{0.19}P_{0.06}Bi_{0.04}$	$MoV_{0.26}Nb_{0.36}P_{0.02}Te_{0.08}$
Particle 3	$MoV_{0.15}Nb_{0.46}\ P_{0.04}$	$MoV_{0.17}Nb_{0.42}P_{0.07}Sb_{0.08}$	$MoV_{0.16}Nb_{0.30}P_{0.05}Bi_{0.05}$	$MoV_{0.21}Nb_{0.38}P_{0.02}Te_{0.08}$
Particle 4	$MoV_{0.19}Nb_{0.49}\ P_{0.04}$	$MoV_{0.07}Nb_{0.06}P_{0.05}Sb_{0.13}$	$MoV_{0.16}Nb_{0.31}P_{0.05}Bi_{0.05}$	$MoV_{0.28}Nb_{0.37}P_{0.04}Te_{0.08}$

niobium oxalate (CBMM), and the corresponding aqueous salt of Te, Bi or Sb [15]. The resulting gels, with a Mo/V/Nb/P/X (X=Te, Bi or Sb) atomic ratio of 1/0.20/0.17/0.08/0–0.04, were incorporated to a Teflon-lined, stainless steel autoclave and heated at 175 °C for 48 h. The solid obtained is filtered off, washed and dried at 80 °C for 16 h. Finally, the solids were heat-treated at 700 °C in flowing N_2 for 2 h. The catalysts will be named as TB-O (for the undoped) and TB-x (x=Te, Bi or Sb, for the corresponding promoted samples).

2.2. Catalyst characterization

The surface areas of the catalysts were measured on a Micromeritics ASAP 2000 instrument by adsorption of krypton.

Powder X-ray diffraction was used to identify the crystalline phases present in the catalyst. An Enraf Nonius FR590 sealed tube diffractometer, with a monochromatic Cu Kα1 source operated at 40 kV and 30 mA was used. XRD patterns were calibrated against a silicon standard and phases were identified by matching experimental patterns to the JCPDS powder diffraction file.

Infrared spectra were recorded at room temperature in the 300–3900 cm^{-1} region with a Nicolet 205xB spectrophotometer, equipped with a Data Station, at a spectral resolution of 1 cm^{-1} and accumulations of 128 scans.

Scanning electron microscopy (SEM) and EDX microanalyses were performed on a JEOL JSM 6300 LINK ISIS instrument. The quantitative EDX analysis was performed using an Oxford LINK ISIS System with the SEMQUANT program, which introduces the ZAF correction. Catalysts chemical compositions are shown in Table 1.

2.3. Catalytic experiments

Catalytic activity in the olefin oxidation was measured using a fixed bed laboratory micro-reactor, at atmospheric pressure, in the temperature range 360–380 °C. The feed, with a total flow rate of 25–50 ml min^{-1}, corresponds to a mixture consisting of olefin/O_2/He/H_2O with a molar ratio of 1.7/6.8/76.5/15. Reactants and reaction products were analysed using two chromatographs: (i) an on-line chromatograph with a Thermal Conductivity Detector containing two chromatographic columns (Molecular Sieve and Porapak Q) to analyse the carbon oxides, oxygen, propylene and oxygenates products; and (ii) an off-line chromatograph with a Flame Ionization Detector equipped with a capillary column (Plot Alumina, 50 m) to provide a better analysis of C_4–olefins. Mass spectrometry was also used in order to determine the appearance of minority products. The carbon balance was estimated with an accuracy of ±4%. Blank experiments were conducted in an empty reactor at 380 °C and using a total of 25 ml min^{-1}. If propene was the hydrocarbon fed the activity observed was negligible. Using isobutene or 1-butene an olefin conversion lower than 2% was observed.

3. Results and discussion

3.1. Catalyst characterization

After calcination, dark-brown to purple bronzes with very low surface area (about 5.0 $m^2\ g^{-1}$) and metallic sheen are obtained.

EDX analysis (Table 1) shows a very homogeneous composition for all crystals based on Mo–V–Nb–P. At this point, we have to emphasize the constant presence of phosphorous in all materials and particles, with an atomic ratio about 5.0%, thus, close to that of the original heteropolyacid. According to ^{31}P-NMR results (J.M. López-Nieto et al., to be published), phosphorous is incorporated in the structure of the bronze as tetrahedral PO_4 monophosphate or diphosphate.

Fig. 1 shows the XRD patterns of all the catalysts tested. In all of them typical peaks of the TTB-type structure have been observed at diffraction angles $2\theta = 22.2°, 23.3°, 26.6°, 30.5°, 33.2°$ and $35.0°$. In the case of the unpromoted and Te-promoted catalysts the only

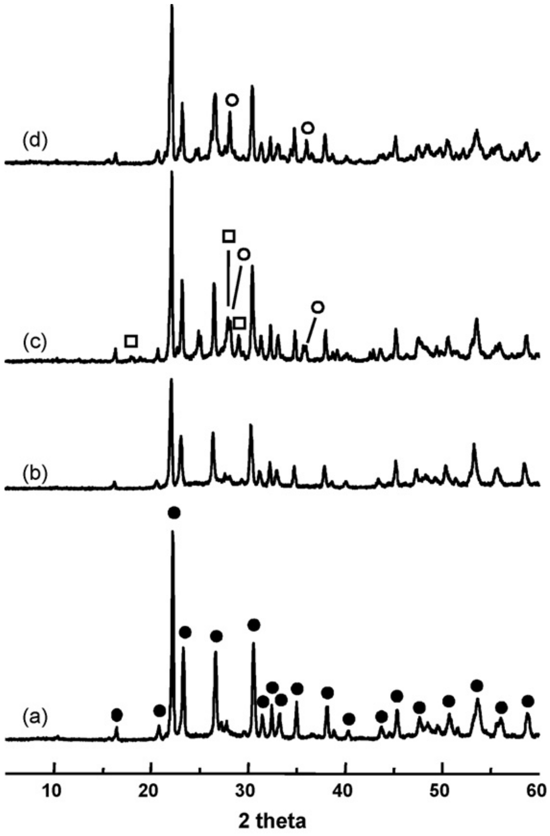

Fig. 1. XRD patterns of TTB bronzes: (a) TB-O, (b) TB-Te, (c) TB-Bi and (d) TB-Sb. Symbols: main reflections of TTB crystal phase (●); $(Sb_2O)M_6O_{19}$ or $Bi_{0.33}MO_{3.33}$ (M= Mo, V, Nb) also called M2-phase (○); $Bi_2Mo_3O_{12}$ (□).

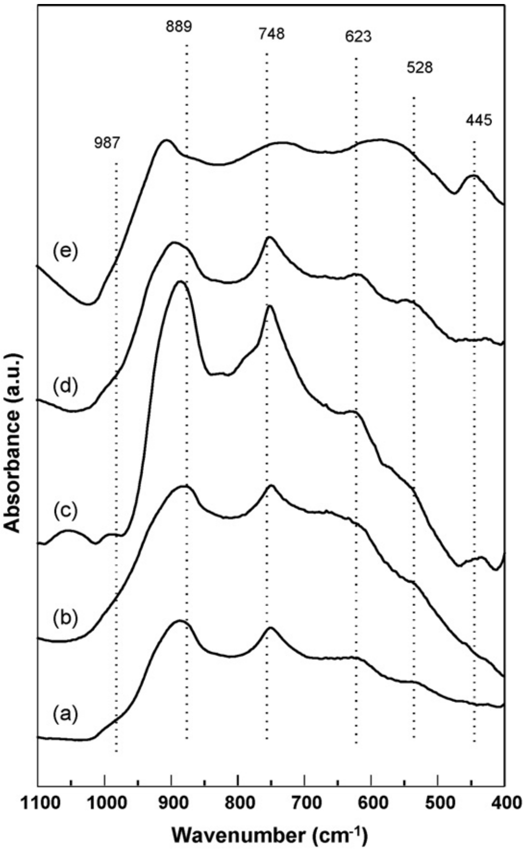

Fig. 2. FTIR spectra of TTB bronzes: (a) TB-O, (b) TB-Te, (c) TB-Bi and (d) TB-Sb. For comparison the IR spectra of a MoVTe hexagonal bronze (M2-phase) is also included.

crystalline phase identified has been the TTB-type structure [15]. In the case of Bi- and Sb-containing catalysts the main phase is the TTB-type structure although reflections corresponding to $Bi_2Mo_3O_{12}$ [JCPDS: 21-0103] or the hexagonal bronze $(Sb_2O)M_6O_{19}$ [16] or $Bi_{0.33}MO_{3.33}$ (M=Mo, V, Nb), have also been observed as minorities.

Infrared spectra of catalysts are presented in Fig. 2. All samples present a shoulder at 987 cm^{-1} and two intense broad bands at 889 and 748 cm^{-1}, in addition to bands at 623, 528 and 445 cm^{-1}. If we compare these IR spectra with those previously reported for Mo-containing bronzes with a different crystalline structure, i.e., $Te_{0.33}MO_{3.33}$ (M=Mo, V, Nb) [16], Nb-doped Mo_5O_{14} [17] or $Mo_3Nb_2O_{14}$ [18], it can be concluded that the high-frequency bands are related to Mo=O double bond stretching vibrations, while the lower-frequency bands are related to Mo–O–Y (Y=V, Nb, as well as Te, Sb or Bi) bridge vibrations.

It has been proposed that bands at ca. 750 cm^{-1} could be attributed to the Nb–O–Mo symmetric vibrations in $Mo_3Nb_2O_{14}$ [18,19]. Accordingly, the band at 748 cm^{-1} in Fig. 2 should be related to such Nb–O–Mo vibration.

3.2. Catalytic tests for olefin partial oxidation

Table 2 shows comparatively the catalytic results obtained during the oxidation of C_3–C_4 olefins over TTB-based catalysts at a reaction temperature of 380 °C. Different contact times have been employed in order to show comparatively the catalytic results at an olefin conversion of ca. 40%.

In the case of propene oxidation, acrolein, acetone, acetic acid and carbon oxides (CO and CO_2) have been the main reaction products. Acrylic acid and acetaldehyde have also been detected with lower selectivity. Fig. 3a shows the evolution of the selectivity to acrolein with the propene conversion, obtained during the propene oxidation at 380 °C. TB-Te catalyst presents a high selectivity to acrolein (ca. 90%), while the unpromoted sample (TB-O) is unselective to partial oxidation reaction (selectivity lower than 4% is observed). Bi- and Sb-containing catalysts show intermediate selectivity to acrolein (ca. 31% and 8%, respectively). On the other hand, we must inform that acetic acid and acetone were relatively formed on TB-O catalyst in addition to carbon oxides (Table 1). However, they are obtained as minorities in the case of promoted catalysts.

In the case of isobutene oxidation, methacrolein, acetone, acetic acid and carbon oxides have been the main reaction products observed in all catalysts (Table 2). Fig. 3b presents the variation of the selectivity to methacrolein with the isobutene conversion obtained at 380 °C. The highest selectivity to methacrolein has been obtained over the Te-containing catalyst. For the rest of the catalysts the selectivity to methacrolein followed the same trend than that observed for the selectivity to acrolein from propene: TB-Te > TB-Bi > TB-Sb > TB-O. It is noteworthy that the selectivity to methacrolein of ca. 80% was kept in a wide range of isobutene conversions (even until 90%, not shown here) over the Te-containing catalyst (TB-Te).

For 1-butene oxidation, butadiene, *cis*- and *trans*-2-butene, acetone, acetic acid and carbon oxides were mainly observed. No partial oxygenated product without a break of the C–C bond has been observed. Figs. 4 and 5 plot the evolution of the selectivity to butadiene (Fig. 4a), 2-butenes (Fig. 4b) and CO_x (Fig. 5) with the 1-butene conversion. The selectivity to butadiene decreases following the order (Fig. 4a): TB-Te > TB-Bi > TB-Sb > TB-O, while

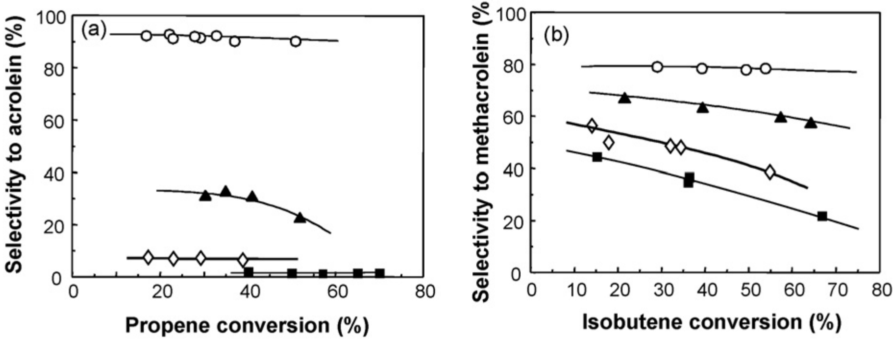

Fig. 3. Variation of the selectivity to acrolein (a) and methacrolein (b) with the corresponding olefin conversion obtained during the oxidation of propene or isobutene, respectively, over TTB-bronze catalysts. Reaction temperature = 380 °C. The contact time has been modified to achieve different hydrocarbon conversions. Symbols: TB-Te (○); TB-Bi (▲); TB-Sb (◇); TB-O (■).

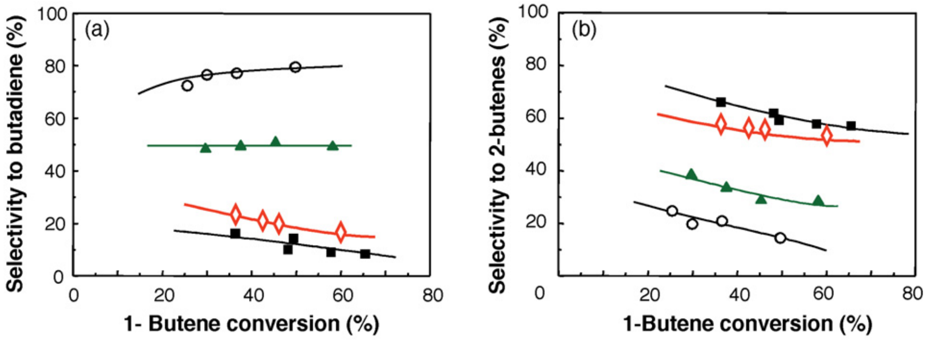

Fig. 4. Variation of the selectivity to butadiene (a) and 2-butenes (b) with the 1-butene conversion obtained during the oxidation of 1-butene over TTB-bronze catalysts. Reaction temperature = 380 °C. The contact time has been modified to achieve different hydrocarbon conversions. Symbols: TB-Te (○); TB-Bi (▲); TB-Sb (◇); TB-O (■).

the isomerization of 1-butene to 2-butene follows an opposite trend (Fig. 4b). We must indicate that the selectivity to butadiene increases with the 1-butylene conversion reaching a selectivity of 80% for the Te-containing catalyst (TB-Te).

Table 3 shows comparatively the catalytic activity for olefin oxidation (propene, isobutene and 1-butene) of TTB-based catalysts. The catalytic activity for olefin oxidation decreases in the following order: TB-O > TB-Bi > TB-Sb, TB-Te (Table 3).

These catalytic results are in agreement to previous results obtained over molybdate-based catalysts in which selective catalysts for partial oxidation of propene to acrolein are also very selective in the partial oxidation of both 1-butene to butadiene and isobutene to methacrolein [20–23]. Thus, catalysts based in TTB-bronzes seem to have a catalytic behaviour similar to that observed in other molybdate-based catalysts. The incorporation of elements of the groups V and VI to MoVNbPO catalyst with TTB-structure modifies strongly both the catalytic activity and the selectivity to partial oxidation products, although the catalytic performance depends on the promoter added and the olefin fed.

3.3. On the role of promoters on the selectivity to partial oxidation products

For all the olefins tested there are two clear extreme patterns of behaviour and therefore, we will focus our discussion in both catalysts: (i) the catalyst without the incorporation of any element of the V and VI groups and, i.e., TB-O sample *t*, which presents a very low selectivity to partial oxidation products; and (ii) the Te-containing catalyst, i.e., TB-Te sample, which presented the higher selectivity to partial oxidation products (acrolein from propene, methacrolein from isobutene and butadiene from 1-butene). The performance of Bi- or Sb-containing catalysts was intermediate between that of TB-O and TB-Te catalysts. It must also be mentioned that acetone and/or acetic acid were observed during the oxidations of all the olefins tested and their selectivities decrease as follows: TB-O > TB-Sb > TB-Bi > TB-Te.

It has been proposed that the presence of acid sites in molybdate-based catalysts favours the isomerization of 1-butene to 2-butene (on Brönsted acid sites) or the deep oxidation of 1-butene (on Lewis acid sites), while the elimination of these acid sites favours the oxidative dehydrogenation of 1-butene to butadiene [20,21,24]. On the other hand, it is also known that the presence of acid sites in addition to redox sites, as in Mo–V-based catalysts, favours the oxyhydrative scission of olefins (with the formation of acetone and acetic acid) rather than the selective oxidation of olefins [25–28]. However, carbon oxides are mainly formed on catalysts presenting only acid sites [24,27]. For this reason, the reaction products obtained during the 1-butene

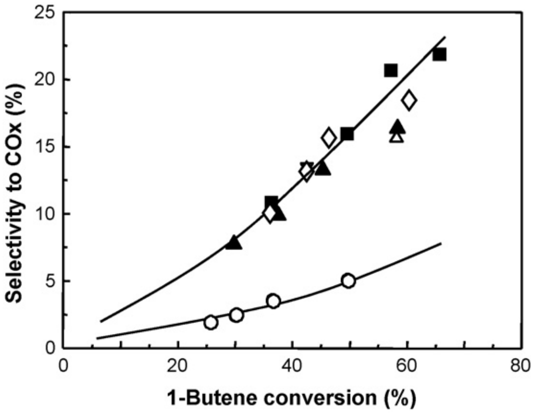

Fig. 5. Variation of the selectivity to carbon oxide with the 1-butene conversion obtained during the oxidation of 1-butene over TTB-bronze catalysts. Reaction conditions and symbols as in Fig. 4.

Table 2
Partial oxidation of propylene, isobutene and 1-butene over TTB bronzes at 380 °C

Catalyst	TB-O	TB-Sb	TB-Bi	TB-Te
C_3H_6 oxidation				
(W/F)[a]	(500)	(2000)	(1000)	(2000)
Conversion (%)	39.8	36.9	41.1	36.6
Selectivity (%)[b] to				
Acrolein	1.5	6.8	30.9	90.8
Acetone + acetic acid	20.8	8.4	7.4	1.5
$CO + CO_2$	73.8	82.7	56.4	6.5
i-C_4H_8 oxidation				
(W/F)[a]	(60.0)	(400)	(200)	(400)
Conversion (%)	36.6	44.0	39.5	39.3
Selectivity (%)[b] to				
Methacrolein	34.4	43.3	62.8	78.4
Acetone + acetic acid	15.1	10.1	7.0	3.2
$CO + CO_2$	51.0	46.6	44.3	18.4
1-C_4H_8 oxidation				
(W/F)[a]	(40)	(300)	(200)	(400)
Conversion	48.2	46.1	45.4	39.8
Selectivity (%)[b] to				
Butadiene	10.1	16.4	50.7	78.5
2-Butene (*cis*/*trans*)	61.9	55.3	28.6	16.5
Acetone + acetic acid	8.6	6.9	4.6	1.1
$CO + CO_2$	18.0	15.9	13.2	3.8

[a] Different contact times (W/F, in g_{cat} h mol_{olefin}^{-1}) were employed in order to achieve olefin conversions of ca. 40%.

[b] Traces of other products were also detected.

Table 3

Catalytic activity of TTB-based catalysts in the oxidation of C_3–C_4 olefins[a]

Catalyst	Catalytic activity (g_{olefin} / ($kg_{catalyst}$ h))			
	Propene oxidation	Isobutene oxidation	1-butene oxidation	
			Oxidation[b]	Oxidation + isomerization[c]
TB-O	62	475	360	939
TB-Sb	15	86	54	120
TB-Bi	32	154	126	177
TB-Te	14	77	65	78

[a] Data at 380 °C.

[b] Considering only oxidation products (butadiene, acetone, acetic acid and carbon oxides).

[c] Considering both oxidation and isomerization products (butadiene, acetone, acetic acid, 2-butenes and carbon oxides).

oxidation can be used as a direct probe to know the characteristics of catalysts.

The catalytic results for 1-butene oxidation in Fig. 4b suggest that the isomerization of 1-butene decreases in the order (Fig. 4b): TB-O > TB-Sb > TB-Bi > TB-Te, while the oxidative dehydrogenation of 1-butene shows an opposite trend (Fig. 4a). In this way, the oxidation/isomerization ratio during the 1-butene oxidation (calculated from the corresponding catalytic activities in Table 2) decreases as follow: TB-Te (5.0) > TB-Bi (2.5) > TB-Sb (0.82) > TB-O (0.61).

On the other hand, the catalytic results obtained during the oxidation of propene or isobutene, but also with 1-butene (Table 2), indicate that the formation of acetic acid is more favoured on the unpromoted catalyst and less favoured over TB-Te catalysts, showing an intermediate behaviour in the case of Bi- or Sb-containing catalysts.

Fig. 5 shows the variation of the selectivity to CO_x with the 1-butene oxidation obtained over unpromoted and promoted samples. It can be seen that the Te-containing catalyst presents the lowest formation of carbon oxides, while there are not differences in the selectivity to carbon oxides obtained on the rest of the TTB catalysts. Thus, the role of Te^{4+} should be related not only with the blockage of Brönsted acid sites (thus, favouring a drop in the isomerization process) but also with the elimination of deep oxidation sites. In contrast, the incorporation of Bi^{3+} or Sb^{3+} permits an important decrease in the isomerization of 1-butene to 2-butene with respect to the undoped sample, but no modification in the deep oxidation of 1-butene is observed.

According to previous studies on molybdate-based catalysts, the incorporation of Te, Bi or Sb ions favours an elimination of surface acid sites, thus favouring an allylic mechanism that takes place on redox sites [21,29,30]. So, the same conclusion can be proposed in the case of the incorporation of these elements in bronze-based catalysts. However, the efficiency of these elements as promoters in the selective oxidation of C_3–C_4 olefins seems to be slightly different.

At this point, it could be interesting to compare the catalytic performance of promoted TTB catalysts with those observed over Te- or Sb-based catalysts with a hexagonal structure, i.e., $Te_{0.33}MO_{3.33}$ and $(Sb_2O)M_6O_{19}$ (M=Mo, V, Nb). $Te_{0.33}MO_{3.33}$ is active and selective in the oxidation of propene to acrolein/acrylic acid [16], while $(Sb_2O)M_6O_{19}$ presents a lower selectivity to acrolein [31].

In the same way, the selectivity to acrolein during the propene oxidation over $TeMo_5O_{16}$ is relatively higher than those observed over $Bi_4Mo_{20}O_{63}$ or $Sb_4Mo_{20}O_{62}$ [32,33], suggesting that the incorporation of Te^{4+} ions in TTB-bronzes or other partially reduced structures have a promoter effect for selective oxidation reactions higher than that for the corresponding Sb-containing bronzes, with Bi^{3+}-promoted ones presenting a catalytic intermediate behaviour between Te^{4+} and Sb^{3+}.

Accordingly, an α-hydrogen-abstracting site (Te^{4+}, Bi^{3+}, Sb^{3+}) and an O-insertion site (Mo^{6+}) in a well defined host structure are needed to achieve the H-allylic mechanism for partial oxidation of olefins. However, the drastic elimination of non-selective sites observed in the 1-butene oxidation over Te-promoted catalysts is not completely observed in the other promoted catalysts (Fig. 5).

3.4. On the importance of the olefin fed

A second important aspect to be considered from the comparison of the catalytic behaviour of these catalysts is related with the differences observed for the selectivity to partial oxidation products depending on the olefin fed. For better discussion we will compare the catalytic results obtained during the oxidation of propene (Fig. 3a) and isobutene (Fig. 3b). In the case of Te-catalysts, the selectivity to the corresponding aldehyde (at an olefin conversion of 50%) is ca. 90 (acrolein) and ca. 80% (methacrolein). For the Bi-containing catalyst, the corresponding selectivity, at the same reactions conditions, was ca. 25% (acrolein) and ca. 65% (methacrolein). In the case of the unpromoted catalyst, TB-O, the selectivities were ca. 1% (acrolein) and ca. 25% (methacrolein). Therefore, it seems clear that the olefin fed influences the selectivity to partial oxidation products.

Table 3 shows comparatively the catalytic activity obtained during the oxidation of C_3–C_4 olefins. It can be seen that the catalytic activity decreases as: isobutene > 1-butene > propene. This order is in good agreement with the heats of adsorption of these olefins on the surface of Mo-based catalysts as well as their reactivity in oxidation reactions [20–23,33–38].

An increase in the reactivity of the olefin has been reported to favour a higher reduction of the catalyst surface and it has been related to an increase in the formation of partial oxidation products. Thus, one could expect that the reduction degree of catalysts during the oxidation of isobutene or 1-butene must be higher than during the propene oxidation. In this way, a higher catalyst reduction degree [33] when working with isobutene than with propene can be expected since the reactivity [23,34] and the irreversible adsorption are higher in the case of isobutene [35–37] than in propene. In this way, we must indicate that the selectivity to partial oxidation products (unsaturated aldehydes or conjugated dienes) over Bi- or Sb-containing catalysts is (Table 1): methacrolein > butadiene > acrolein; while in the case of Te-containing catalysts is: acrolein > butadiene > methacrolein. Accordingly, the relatively less selective catalysts in the propene oxidation to acrolein are more selective during the isobutene oxidation. Therefore, some differences in the promoter effect of the metal added must be taking place depending on the olefin fed and the redox properties of catalysts.

4. Conclusions

Mo-V-Nb-P-O-based catalysts with a TTB-type structure prepared hydrothermally from Keggin-type phosphomolybdic acid are active but unselective in the partial oxidation of olefins. However, the incorporation of Te, Sb or Bi in the synthesis gel favours a higher selectivity to partial oxidation products during the oxidation of olefins. The bronze with tellurium resulted to be the most efficient for all olefins tested, i.e., propene, isobutene and 1-butene.

The catalytic results can be explained by the promoter effect of Te ions, and in a lower extension of Bi or Sb ions, in a similar way to that proposed in the case of molybdate-based catalysts. Moreover, the selectivity to partial oxidation products depends on both the promoter added and the olefin tested.

Acknowledgments

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