The hydrothermal synthesis of tetragonal tungsten bronze-based catalysts for the selective oxidation of hydrocarbons†

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Mixed metal oxides with tetragonal tungsten bronze (TTB) structure, showing high activity and selectivity for the gas phase partial oxidation of olefins, have been prepared by hydrothermal synthesis from Keggin-type heteropolyacids.

MoVTe(Sb)NbO oxidic bronze catalysts initially reported by Mitsubishi[1] are promising catalysts in the (amm)oxidation of propane[1,2] and in the oxidative dehydrogenation of ethane.[3] Generally speaking, they mainly constitute two crystal phases:[1–5] the orthorhombic $Te_2M_{20}O_{57}$ (M = Mo, V, Nb; the so-called M1) and the pseudohexagonal bronze $Te_{0.33}MO_{3.33}$ (M = Mo, V, Nb; the so-called M2). The M1 phase is active and selective in the partial oxidation of propane or ethane, while M2 is only active and selective in the oxidation of propene to acrolein and/or acrylic acid.[2–6] Moreover, the synthesis procedure strongly influences both physicochemical and catalytic performance.[1–7] It has been suggested that these transition metal composite oxides could be prepared by self-organization of polyoxometalates,[2b] these being MoVTe(Sb)NbO oxides obtained from slurries prepared with Anderson heteropolyacids.[2b,3–6] Anderson heteropolyacids have also been employed in the hydrothermal synthesis of these materials, although orthorhombic[3,5,6] or trigonal[7] phases were obtained depending on specific synthesis conditions. It has been suggested that the Mo-intermediate formed during the hydrothermal synthesis[7] could be similar to those proposed by Muller *et al.*[8] in the preparation of giant polyoxomolybdates.

During the last few years several groups have been working on the synthesis of new similar materials. Among these new materials, we can highlight the heat-treated pyridine and niobium molybdovanadophosphoric acid based catalysts, active and selective in the partial oxidation of light alkanes,[9] or new Cs-containing M1-phase oxides, active and selective in the partial oxidation of C_3–C_4-olefins.[10] Recently, we reported that mixed metal oxides prepared from Keggin-type heteropolyacids could be used as catalysts in the selective oxidation of hydrocarbons.[11] The present work shows how the hydrothermal synthesis from Keggin-type heteropolyacids can facilitate the preparation of Mo(W)VNbO mixed oxides with a tetragonal tungsten bronze (TTB) structure, and how the catalytic performance in the partial oxidation of olefins of these solids is completely modified when trivalent and tetravalent elements of the V and VI groups are present in the hydrothermal process. In addition, it will be shown that the catalytic performance of this crystalline phase can be tailored by changing the composition of both the heteropolyacid precursor and the synthesis gel.

Mo- and/or W-containing TTB-type phases were prepared by hydrothermal synthesis using a polyoxometalate, niobium oxalate, vanadyl sulfate, and a X-metal oxide (X = Te, Sb or Bi) with a (Mo,W)/Nb/V/X atomic ratio of 1/0.17/0.20/x (x = 0 to 0.08) and a (Mo,W)/H_2O molar ratio of 1/87. The gels were loaded in Teflon-lined stainless-steel autoclaves and heated at 175 °C for 48 h. The resulting solids were dried at 80 °C for 16 h, and calcined in the 700–800 °C temperature range during 2 h in a N_2-stream. The synthesized catalysts were tested in a fixed bed quartz reactor, at reaction temperatures ranging from 300 to 400 °C and atmospheric pressure. The reaction feed consisted of a mixture of propene–oxygen–steam–helium with a molar ratio of 1.5/6/15/77.5. The catalytic tests refer to steady-state conditions; no deactivation was observed over about 100 h. A blank run showed that under our reaction conditions the homogeneous process could be neglected.

Fig. 1 shows some characterization results of sample H1-T (Table 1). The powder X-ray diffraction pattern of calcined sample shows the formation of a high purity TTB-related crystal phase (Fig. 1a). This has been observed in all prepared catalysts independently of the heteropolyacid precursor and/or the chemical composition.[12] Fig. 1b corresponds to the electron diffraction pattern of the same sample. Diffuse scattering around the main TTB reflections is indicative of a short range order situation which is clear from the observation of the corresponding electron micrograph in Fig. 1c. Moreover, the structural characterization suggests that the microstructure of these Mo- or W-containing TTB-bronzes depends on the final niobium content.[13,14]

The final calcination temperature required in the formation of crystalline phases depends on the catalyst composition (Table 1). Thus, it has been observed that W-based catalysts need heat-treatment temperatures higher than the corresponding Mo-based catalysts. On the other hand, no significant differences in their XRD patterns were observed in solids prepared in the presence or absence of elements of the V and VI groups in the X/(Mo + W) atomic ratio of 0 to 0.10. However, it is important to mention that the presence of these elements in the W-based catalysts favours a decrease in the calcination temperature needed to obtain the tetragonal bronze.

We must indicate that no TTB bronzes but a mixture of M_5O_{14}-type phases and single oxides (basically MoO_3) were obtained when phosphoric acid and ammonium heptamolybdate (or

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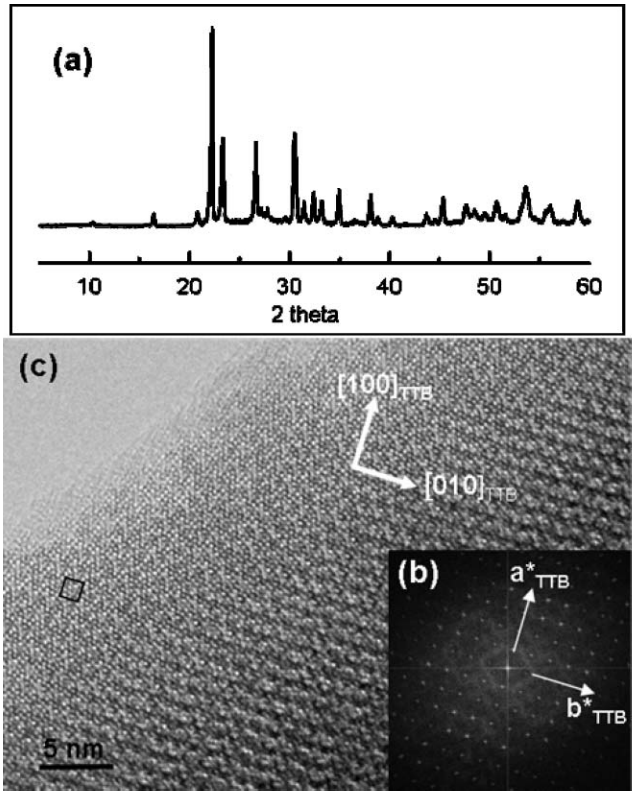

Fig. 1 Powder XRD pattern (a), FFT on the $[001]_{TTB}$ zone axis (b) and corresponding HREM micrograph of a crystal of sample H1-T (c).

ammonium tungstate) were used as reactants instead of the corresponding Keggin-type polyoxometalate. On the other hand, the results obtained at the moment suggest that Si-containing heteropolyacids seem to favour the formation of solids with less purity than the corresponding P-containing ones.

Table 1 presents comparatively the catalytic performance obtained during the partial oxidation of propene over Mo- and/or W-based TTB oxides. Active but unselective catalysts were obtained when tetrahedral bronzes were prepared in the absence of elements of the V and VI groups. In these cases, acetic acid was the only partial reaction product, as has also been observed in other oxidic bronzes without these elements.[15] Moreover, active and selective catalysts for the selective oxidation of propene to acrolein and/or acrylic acid are obtained in the corresponding Te-, Sb-, or Bi-containing tetragonal bronzes, although the selectivity to partial oxidation products decreases in the order: Te-based catalysts > Sb-based catalysts > Bi-based catalysts (Table 1). These results show a similar trend to those observed in M1/M2-based catalysts, in which the metal incorporated in the hexagonal channels (*i.e.* Te^{4+} or Sb^{3+}) strongly influences their catalytic behaviour.[2,5,7] Accordingly, the tetragonal bronzes presented here have a catalytic performance similar to that observed for the pseudohexagonal bronzes (the so-called M2 phase), although some of them are more active for propene partial oxidation (Table 1).

The high selectivity to partial oxidation products obtained on Te-containing Mo-TTB bronzes must be emphasized. In this case a selectivity to acrolein + acrylic acid of *ca.* 90% has been achieved in a wide range of propene conversions: i) acrolein is almost the only partial oxygenated product at low propene conversions; and ii) acrolein is partially transformed into acrylic acid at high propene conversions (Table 1).

Nevertheless, it can be noticed that W–Te-based catalysts (sample H2-T) are clearly more active but less selective to the formation of partial oxidation products than the corresponding Mo–Te-based catalyst (H1-T). Thus, one way to optimize the catalytic system based on TTB-type structure could be the synthesis of materials containing both Mo and W. For this purpose, a mixture of phosphomolybdic and phosphotungstic acids with a 1 : 1 molar ratio was used for the preparation of the corresponding mixed metal oxide. The final catalyst H4-T presented the characteristic XRD pattern of the tetragonal bronze,[12] while the SEM-EDS analysis showed that both Mo and W were homogeneously distributed and with a similar ratio to the one introduced in the initial synthesis gel. This catalyst presented propene conversions higher than those observed for

Table 1 Partial oxidation of propene at 380 °C over Mo- and/or W-containing TTB bronzes[a]

	Catalyst synthesis				Propene oxidation				
						Selectivity (%)[h]			
Sample[b]	Precursor[c]	X/(Mo + W) (atomic ratio)[d]	$T_{calc.}$ (°C)[e]	Chemical composition (atomic ratio)[f]	Conversion (%)[g]	Acrolein	AA	CO_x	Other
H1	PMo_{12}	0	700	$MoNb_{0.44}V_{0.18}P_{0.09}$	57.8	2.2	0.9	74.6	22.3
H1-T	PMo_{12} (TeO_2)	0.04	700	$MoNb_{0.56}V_{0.17}P_{0.1}Te_{0.15}$	22.3	91.7	1.6	2.9	3.8
H1-T2	PMo_{12} (TeO_2)	0.08	700	$MoNb_{0.39}V_{0.17}P_{0.02}Te_{0.23}$	69.0[i]	55.0	35.8	8.4	0.8
H1-S	PMo_{12} (Sb_2O_3)	0.04	700	$MoNb_{0.27}V_{0.11}P_{0.11}Sb_{0.11}$	23.3	6.6	0	69.3	24.1
H1-B	PMo_{12} (Bi_2O_3)	0.04	700	$MoNb_{0.37}V_{0.14}P_{0.14}Bi_{0.32}$	35.0	32.8	1.6	49.4	16.2
H2	PW_{12}	0	800	$WNb_{0.82}V_{0.28}P_{0.05}$	31.7	0.9	0	96.9	2.2
H2-T	PW_{12} (TeO_2)	0.04	700	$WNb_{0.69}V_{0.25}P_{0.05}Te_{0.23}$	36.4	65.7	2.4	30.0	1.9
H3	$SiMo_{12}$	0	700	$MoNb_{0.28}V_{0.18}Si_{0.07}$	61.5	0.5	0	86.4	13.1
H3-T	$SiMo_{12}$ (TeO_2)	0.04	700	$MoNb_{0.19}V_{0.19}Si_{0.07}Te_{0.01}$	34.8	68.3	14.9	12.6	4.2
H4-T	PMo_{12} + PW_{12} (TeO_2)	0.04	700	$Mo_{0.55}W_{0.45}Nb_{0.56}V_{0.21}P_{0.07}Te_{0.06}$	62.2	79.3	10.9	7.4	2.4

[a] Reaction conditions: contact time, W/F, of 550 g_{cat} h/mol_{C3}; $C_3/O_2/He/H_2O$ molar ratio of 1.5/6/77.5/15. [b] H1-T, H1-S, H1-B are catalysts with X = Te, Sb or Bi, respectively. [c] Heteropolyacid used in the hydrothermal synthesis (in brackets, metal oxide of the V or VI group element when incorporated): $H_3PMo_{12}O_{40}$ (PMo_{12}); $H_3PW_{12}O_{40}$ (PW_{12}). [d] X/(Mo + W) atomic ratio in the hydrothermal synthesis (X = Te, Sb or Bi). [e] $T_{calc.}$, calcination temperature of catalysts. [f] As determined by ICP analysis in the calcined samples. [g] Propene conversion (%). [h] Selectivity to acrolein, acrylic acid (AA), CO + CO_2 (CO_x) and other partial oxidation products (acetic acid, acetone and acetaldehyde). [i] Reaction conditions: reaction temperature = 420 °C; contact time, W/F, of 1900 g_{cat} h/mol_{C3}; $C_3/O_2/He/H_2O$ molar ratio of 1.5/6/77.5/15.

Mo–Te-based catalysts with similar selectivities to partial oxidation products, suggesting a promotion effect when both elements (Mo and W) are present in the catalyst.

These catalysts were also active in the partial oxidation of isobutylene. Thus, a selectivity to methacrolein of *ca.* 80% at an isobutylene conversion of 90% was achieved over the Mo–Te-based catalyst (H1-T), while the rest of the catalysts presented a catalytic behaviour similar to that observed for propene oxidation.

In conclusion, we have prepared a new type of W- and specially Mo-containing catalysts with a TTB-type structure, which are active and selective in the partial oxidation of olefins. Moreover, the heteropolyacid precursor seems to be a key factor in the nature of the final crystal structure obtained, in agreement with previous results presenting the synthesis of other oxidic bronzes prepared from Anderson type heteropolyacids.[2b,7] However, the role of Te ions in partial oxidation is in agreement with that previously proposed for M1/M2 phase containing catalysts,[1–7] although it will be interesting to study the possible role of the tunnels size (pentagonal in TTB bronzes and hexagonal in M1/M2-containing catalysts) in the catalytic performance. In addition, these TTB-type oxides show great potential as co-catalysts in highly selective catalytic systems for the partial oxidation of hydrocarbons.

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