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Journal of Catalysis 233 (2005) 234–241
JOURNAL OF CATALYSIS
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Synergetic effect between phases in MoVTe(Sb)NbO catalysts used for the oxidation of propane into acrylic acid

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Received 12 October 2004; revised 30 November 2004; accepted 2 December 2004
Available online 3 June 2005

Abstract

Results are reported concerning the synergetic effect observed in the oxidation of propane to acrylic acid over the orthorhombic *M1* and hexagonal *M2* phases present in the most active and selective MoVTe(Sb)NbO catalysts. The pure phases and phase mixtures containing either tellurium or antimony have been prepared and individually tested as catalysts. The results obtained confirm that the phase responsible for the catalytic properties of the efficient catalysts is phase *M1*, and that *M2* is poorly active. Mechanical mixtures of the pure phases have also been prepared and tested. All of the catalysts have been characterized before and after the catalytic reaction by X-ray diffraction, X-ray photoelectron spectroscopy, and high-resolution electron microscopy with EDS analyses. Although the synergetic effect previously described (bifunctional catalysis with the oxidative dehydrogenation of propane molecules on the orthorhombic *M1* phase and the subsequent oxidation of propene on the hexagonal *M2* phase) was observed, another cause related to migration of tellurium from the *M2* phase to the surface of the *M1* phase was indicated. This migration should balance a loss of tellurium in the active phase occurring under the conditions of a catalytic test, but may also create new dehydrogenation sites for propene and/or anneal total oxidation sites. The hexagonal *M2* phase would thus play a role of tellurium reservoir for the active *M1* phase. This effect was not reversible and concerned only the tellurium. Antimony, which is less volatile, should not be lost by the active phase. Furthermore, it was shown not to diffuse at the surface of the phases.

Keywords: Propane mild oxidation and ammoxidation; Synergetic effects; Phase cooperation; MoVTeNb and MoVSbNb oxide catalysts

1. Introduction

In recent years, many investigations have been conducted on multiphasic catalysts used for partial oxidation reaction. One reason for this is the great differences generally observed in catalytic properties between this type of catalysts, which correspond to industrial catalysts, and single-phase catalysts. This improvement of performance for a mixture of phases with respect to each phase component, designated the synergetic effect, has been attributed to different effects [1–4]. These effects have been described as resulting from phenomena as different as bifunctional catalysis, solid-state reaction affecting the bulk phases, surface chemical interaction (migration, contamination), formation of coherent interface, and supporting effect with the spreading of one phase on the other. When experimental evidence for such effects is lacking, a remote effect control mechanism based on an oxygen spillover from one phase to the other has been proposed [5,6]. One of the most spectacular synergetic effects reported is that observed when mixtures of bismuth and cobalt molybdates are used as catalysts in the oxidation and ammoxidation of propene. In this last case, several phenomena have to be considered to explain the synergetic effect: (i) the spread of one phase on the other, (ii) formation of a coherent interphase, and (iii) bifunctional catalysis with the concomitant activation of propene and oxygen on the different phases [7–9].

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doi:10.1016/j.jcat.2004.12.002

Recently very efficient catalysts based on MoVTeNbO mixed oxides have been developed by Mitsubishi for the ammoxidation of propane [10,11]. These catalysts were later claimed to be efficient for several different reactions of alkane oxidation, including oxidation of propane to acrylic acid and oxidative dehydrogenation of ethane [12–14]. The patented catalysts systematically contain several phases; among these, two have been claimed to be necessary for obtaining high performances. These two phases, called *M1* and *M2*, have orthorhombic and hexagonal structures, respectively. The active phase of these catalysts has been proposed to be the phase *M1* [11], and later this was clearly demonstrated when both phases were tested pure [15]. However, the presence of the phase *M2* was shown to improve the selectivity of the catalysts for acrylic acid, even when the biphasic catalysts were prepared from simple mechanical mixtures [16]. This improvement of performances for a mixture of phases with respect to each phase component has been proposed to be related to a bifunctional catalysis, with one phase catalyzing the oxidative dehydrogenation of propane (*M1* orthorhombic) and the other one catalyzing the oxidation or ammoxidation of the formed propene (*M2* hexagonal) [11]. In a recent publication we confirmed this effect on the kinetic data obtained with a prepared mechanical mixture catalyst and extended it to other phase mixtures [15]. More recently, a study by Holmberg et al. [16] of mechanical mixtures of *M1* and *M2* phases containing Te also confirms the existence of the synergetic effect and its bifunctional origin. However, it is difficult to believe that this effect alone can explain the synergetic effect, since it was shown that the active *M1* phase has all the sites needed to transform propane into acrylic acid or acrylonitrile, and it is also very efficient at oxidizing propene to acrylic acid [17,18]; we have therefore undertaken further study of this two-phase system to find other possible origins of the synergetic effect. Moreover, the latter effect did not seem to take place when antimony was substituted for tellurium. We have thus investigated the influence of the ratio of the two phases containing either Te or Sb on the catalytic properties of the mixture, and we have tried to characterize the catalysts by XPS and high-resolution electron microscopy (HREM) with EDS analyses before and after the catalytic reaction to detect a possible transformation of the solids. The results obtained are presented and discussed in this paper.

2. Experimental

2.1. Catalyst preparation

Three types of catalysts were prepared that contained either tellurium or antimony. The first one corresponded to *M1* (orthorhombic) and *M2* (hexagonal) phase mixtures. These compounds were prepared, according to a patented procedure [19,20], from an aqueous slurry comprising Mo, V, Te(Sb), and Nb in the ratio Mo/V/Te(Sb)/Nb = 1:0.33:0.22(0.15):0.11. The slurries were evaporated to dryness at 423 K and successively calcined at 573 K under air and at 873 K under nitrogen for 2 h. In the case of the antimony-containing catalysts, colloidal silica (Ludox) was added to the slurries before the drying step ($\mathrm{Mo/Si} = 0.76$).

The second type of catalysts corresponded to the pure *M1* and *M2* phases. *M1* phases were obtained by treating a *M1* and *M2* phase mixture prepared as described above for 5 h with stirring in a 15% hydrogen peroxide aqueous solution at 298 K. Under such conditions, the *M2* phase was totally dissolved. The *M1* phases were then washed, dried at 383 K, and calcined under nitrogen at 873 K for 2 h. *M2* phases were prepared by solid-state reaction. V_2O_5, TeO_2 or Sb_2O_3, MoO_3, and Mo were mixed in relative proportions corresponding to the theoretical stoichiometry $(Te(Sb)O)_2M_6O_{18}$ ($\mathrm{M} = \mathrm{Mo}$ and V, where $\mathrm{V/Mo} = 0.8$) [21]. The oxide mixtures were sealed in a silica tube under vacuum and heated at 873 K for 72 h. With this preparation procedure it was not possible to synthesize pure Nb-containing *M2* phases. To determine whether the presence of niobium in the *M2* phase was important in the occurrence of a synergetic effect between the *M1* and *M2* phases, we have prepared and studied a *M2* phase containing tellurium and niobium. For that purpose the same protocol was used as for the $M1 + M2$ phase mixtures, but with the starting ratio Mo/V/Te/Nb = 1:0.30:0.41:0.10.

The third type of catalysts corresponded to mechanical mixtures of the prepared pure phases. We obtained these mixtures by mixing the respective powders and hand grinding them for 5 to 10 min. The different phases are referred to here by their type and Nb and Te or Sb contents (*M1*(Sb), *M2*(Nb/Te), *M2*(Sb), etc.). The phase mixtures are denoted as $M1 + M2$(Nb/Te) and $M1 + M2$(Nb/Sb) when they were synthesized and $M1$(Te) + $M2$(Nb/Te) when they were prepared by mechanical mixing.

2.2. Catalyst characterization

Crystal structures of the pure phases and phase mixtures samples were controlled by X-ray diffraction with a Brüker D5005 diffractometer and Cu-K_α radiation. Metal contents of the solids were determined by atomic absorption (ICP), and specific surface areas were measured by the BET method with nitrogen adsorption. XPS measurements were performed with a VG ESCALAB 200 R. Charging of samples was corrected by setting the binding energy of adventitious carbon (C 1s) at 284.5 eV. Deconvolution of the Mo $3d^{3/2}$ peak was accomplished with a Voigt function.

High-resolution electron microscopy was performed with a JEM 2010 ($C\mathrm{s} = 0.5$ mm). Accelerating voltage was 200 kV with a LaB_6 emission current, a point resolution of 0.195 nm, and a useful limit of information of 0.14 nm. The instrument was equipped with an EDS LINK-ISIS (spatial resolution: 1 nm). It allows the use of a probe size of 25 nm to analyze isolated grains of each of the phases and avoid simultaneous analysis of grains of the two phases.

2.3. Oxidation of propane

The oxidation of propane was performed in a fixed-bed reactor operating at atmospheric pressure. The apparatus and the conditions have been described elsewhere [15]. The catalytic properties were determined between 593 and 723 K in a conventional flow reactor with a catalyst amount varying from 0.5 to 1 g. The feedstock composition was $O_2/C_3H_8/Ne/N_2/H_2O = 3{:}1.5{:}1.5{:}10.5{:}13.5$, and the total flow was 30 mL/min.

The reactants and gas products were analyzed with an on-line gas chromatograph and Porapak-Q and CP-Molsieve 5-Å columns. The organic substrates were condensed during the reaction and analyzed off-line [15]. Products formed under the reaction conditions were propylene, CO and CO_2, acrolein, and acetic and acrylic acid. In some cases the formation of acetone was observed. The oxidation of propene has been studied on the phases *M2* by replacing 10% of the propane with propene and running the catalytic test in the same conditions as described above. The catalytic tests were conducted for at least 12 h, and we recovered the catalysts after catalytic testing by cooling them rapidly from 653 K in the flow of reactants.

2.4. Precision

The precision of the chemical analyses and that of the BET surface measurements were evaluated, and both are considered to be 2%. EDS determinations have been made by at least 15 analyses, and standard deviations have been systematically evaluated for atomic ratios. Qualitative analysis of the XPS peaks, in terms of elemental ratios, was carried out as described previously [22]. The experimental precision of the quantitative measurements was considered to be around 15%. The consistency of the catalytic tests has been studied. Carbon balance based on the products listed above was satisfactory in all runs within $100 \pm 2\%$. The standard deviation of the selectivity was estimated to be $\pm 1\%$.

3. Results

3.1. Characterization of the fresh catalysts

The pure-phase Te and Sb samples prepared were confirmed by X-ray diffraction to be single phases, and no phases other than *M1* and *M2* were detected with the same technique in the prepared phase mixtures. The results of the chemical analysis of the synthesized solids are gathered in Table 1. They were in good agreement with the phase stoichiometry reported before [18,21]. All of the solids presented comparably low surface areas. It can be observed that the surface areas of the *M1* phases were always larger than those of the *M2* or *M1* + *M2* phases as synthesized mixtures. The relative content of the synthesized phase mixture was determined from X-ray diffraction patterns. The method used was based on a comparison of the relative surface areas of the peaks at 30.5° 2θ (*M1* phase) and 36.0° 2θ (*M2* phase) in the X-ray diffraction powder patterns [23]. The BET surface area of the *M1* + *M2*(Nb/Te) calculated from the single-phase surface areas and the phase ratio corresponded relatively well with that of the as-synthesized mixture (Table 5). That of the *M1* + *M2*(Nb/Sb) was larger. This difference may be explained by the presence of the small amount of silica added during the synthesis, which contributes to the adhesion of the particles to each other.

3.2. Catalytic activity

3.2.1. Pure phase and phase mixtures obtained from synthesis

The oxidation of propane was conducted at 653 K with the pure *M1* and *M2* phases and with the synthesized phase mixtures. The results obtained with these catalysts are given in Table 2. The *M2* phases, with or without niobium, were almost completely inactive even at 683 K, and it was meaningless to report their catalytic properties. The *M1* phases appeared to be both very active and selective and were unambiguously responsible for the catalytic properties of the synthesized phase mixtures. The properties obtained were comparable to those reported in the literature for Te catalysts and slightly better for Sb catalysts, which are, as for ammoxidation, always less selective [18–20]. The *M1* + *M2*(Nb/Te) phase mixture appeared to be more selective in acrylic acid

Table 1
Chemical analysis and surface area of the synthesized pure phases and phase mixtures

Compound	Chemical analysis	Surface area ($m^2\ g^{-1}$)	$M1/(M1+M2)$
M1(Nb/Te)	$MoV_{0.26}Te_{0.11}Nb_{0.12}$	8.4	
M1(Nb/Sb)	$MoV_{0.28}Sb_{0.13}Nb_{0.15}$	25.1	
M2(Te)	$MoV_{0.4}Te_{0.49}$	0.4	
M2(Nb/Te)	$MoV_{0.30}Te_{0.41}Nb_{0.10}$	3.1	
M2(Sb)	$MoV_{0.49}Sb_{0.29}$	0.3	
M2(Nb/Sb)	$MoV_{0.30}Sb_{0.20}Nb_{0.07}$	9.1	
M1 + *M2*(Nb/Te)	$MoV_{0.30}Te_{0.23}Nb_{0.11}$	4.6	0.45
M1 + *M2*(Nb/Sb)	$MoV_{0.30}Sb_{0.15}Nb_{0.10}$	8.9	0.64

Table 2
Catalytic properties of the *M1* and *M1* + *M2* phases mixtures as synthetized at 653 K; feedstock composition: $O_2/C_3H_8/Ne/N_2/H_2O = 3/1.5/1.5/10.5/13.5$; total flow = 30 mL/min and catalyst mass 0.5 g; AA = acrylic acid, Ace = acetone, and AcA = acetic acid

Compound	Conversion (%)	Selectivities (%)					
		CO	CO_2	AA	C_3H_6	Ace	AcA
M1(Nb/Sb)	35	9	19	49	11	0	11
M1(Nb/Te)	33	9	16	55	11	1	8
M1 + *M2*(Nb/Sb)	34	10	25	41	12	0	12
M1 + *M2*(Nb/Te)	30	7	16	58	11	0	9

Table 3
Catalytic properties of *M2* phases in propene oxidation in presence of propane at 653 K; feedstock composition $O_2/C_3H_8/C_3H_6/Ne/N_2/H_2O$ = 3/1.3/0.2/1.5/10.5/13.5; total flow: 30 mL/min; catalyst mass = 1 g; AA = acrylic acid, Ace = acetone, Acr = acrolein, and AcA = acetic acid

Compound	Conversion (%)	Selectivities (%)					
		CO	CO_2	AA	Ace	Acr	AcA
M2(Sb)	13	0	29	17	11	0	42
M2(Te)	10	0	15	70	0	10	5

Table 4
Catalytic properties of the pure *M1* phases and of the *M1* + *M2* phase mixtures obtained by mechanical grinding; reaction temperature 653 K; feedstock composition $O_2/C_3H_8/Ne/N_2/H_2O$ = 3/1.5/1.5/10.5/13.5; total flow = 30 mL/min; catalyst mass = 1 g for *M1*(Te) + *M2*(Te), *M1*(Te) + *M2*(Sb), and *M1*(Sb) + *M2*(Te), 0.5 g for *M1*(Te) and *M1*(Sb); AA = acrylic acid, Ace = acetone, and AcA = acetic acid

Compound	Conversion (%)	Selectivities (%)					
		CO	CO_2	C_3H_6	AA	Ace	AcA
M1(Nb/Te)	33	9	16	11	55	1	8
M1(Nb/Sb)	35	9	19	11	49	0	12
M1(Nb/Te) + *M2*(Te)	36	3	8	10	74	0	5
M1(Nb/Te) + *M2*(Nb/Te)	37	4	10	9	72	0	5
M1(Nb/Sb) + *M2*(Sb)	36	10	21	11	47	0	11
M1(Nb/Te) + *M2*(Sb)	37	9	17	10	52	0	11
M1(Nb/Sb) + *M2*(Te)	37	9	18	9	59	0	5

than did the *M1*(Nb/Te) phase alone. This result was the opposite of that for the catalysts containing Sb. Because it was proposed that the synergetic effect was related to the fact that the *M2* phase intervened in the transformation of propene formed on the *M1* phase in a manner very selective for acrylic acid [11,12], the pure *M2*(Te) and *M2*(Sb) phases were in the partial oxidation of propene. This was done with the replacement of 10% of the propane with propene in order to run the catalytic test in redox conditions not too different from the initial ones. We observed that both catalysts are active for propene oxidation, but they presented very different selectivities (Table 3). Indeed, the *M2*(Te) phase was very selective for acrylic acid, whereas *M2*(Sb) gave mainly acetic acid.

3.2.2. Phase mixtures obtained by co-grinding

Two types of phase mixtures were prepared by co-grinding of the pure phases and studied. One corresponds to mixtures of phase *M1* and *M2* (with or without Nb) containing either Te or Sb. The other type also corresponds to mixtures of phase *M1* and *M2*, but with one phase containing Te and the other one Sb. The results obtained for the mixtures are compared in Table 4 with those obtained for pure phases at almost the same conversion.

When *M1* and *M2* phase mixtures with the same element (Te or Sb) were compared with the corresponding pure *M1* phases, a synergetic effect was observed only for Te-containing mixtures, with a strong increase in the acrylic acid selectivity for phase mixtures. A decrease in the acrylic acid selectivity was observed for Sb-containing mixtures. It was also observed that the presence or absence of Nb in the *M2* phase has only a small effect on the catalytic properties of the phase mixtures. A slight decrease in acrylic acid selectivity was observed for the phase mixture with a *M2* phase without Nb. This observation is in good agreement with the results obtained when the two *M2* phases were tested for the oxidation of propene [24].

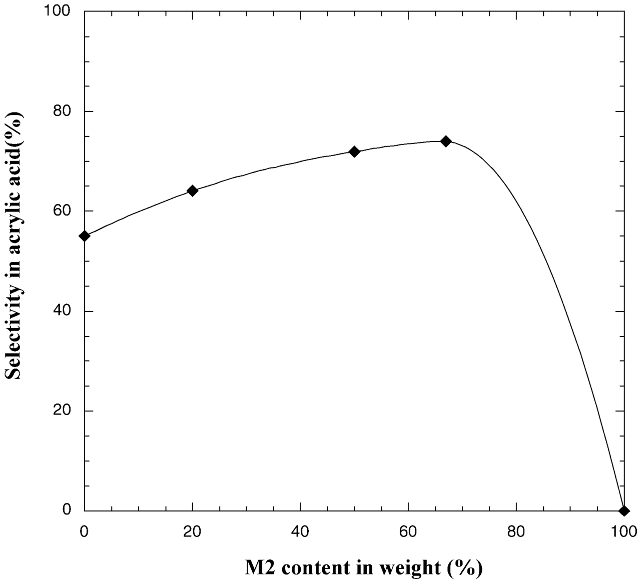

Fig. 1. Variation of the selectivity in acrylic acid at iso-conversion as a function of the *M2*(Te) weight content in the *M2*(Te) + *M1*(Nb/Te) phase mixture. The reaction was run at 653 K; feedstock composition: $O_2/C_3H_8/Ne/N_2/H_2O$ = 3/1.5/1.5/10.5/13.5; total flow = 30 mL/min.

When *M1* and *M2* phase mixtures with different elements (Te or Sb) were compared with pure *M1* phases, a synergetic effect was observed for the *M1*(Nb/Sb) + *M2*(Te) phase mixtures but not for the *M1*(Nb/Te) + *M2*(Sb) phase mixture (Table 4). The selectivity for acrylic acid observed on *M1*(Nb/Sb) + *M2*(Te) increased to 59% to slightly more that of *M1*(Nb/Te) but did not reach that of the *M1*(Nb/Te) + *M2*(Te) phase mixture.

M1(NbTe) + *M2*(Te) phase mixtures with different *M2* (Te) contents have been prepared and tested at isoconversion (35%). Fig. 1 shows the variation in the selectivity for acrylic acid as a function of the *M2*(Te) weight content in the phase mixtures. A maximum yield was obtained for a composition with around 40% *M1*(Te). This composition is different from that patented for phase mixtures obtained by cosynthesis (60%) [25] and that observed (50%) for phase mixtures obtained by co-grinding in the case of ammoxidation [17,18]. The increase in acrylic acid selectivity was plotted for different phase mixtures as a function of the reaction temperature (Fig. 2). We can see that the synergetic effect was observed for all of the reaction temperatures studied between 600 and 658 K and increased with reaction temperature. At the same time its maximum moved from around 50–40% *M1*(Te).

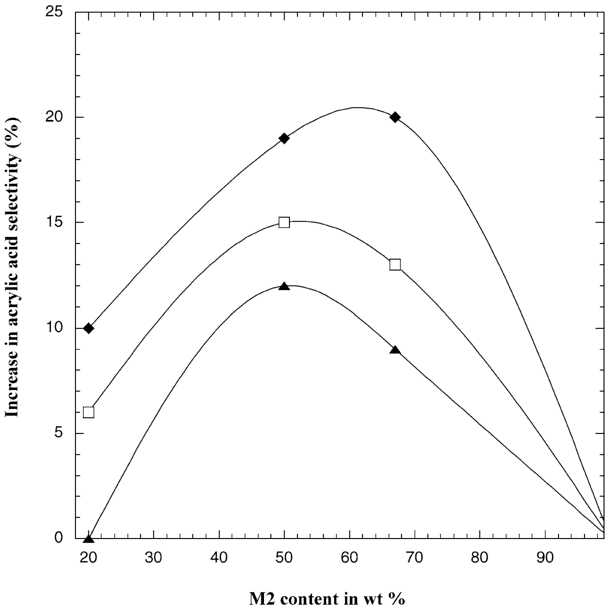

Fig. 2. Evolution as a function of *M2*(Te) phase content of the synergetic effect on the *M1*(Nb/Te) + *M2*(Te) phase mixtures expressed as the increase in acrylic acid selectivity compared that of the pure *M1*(Nb/Te) phase and determined at the same conversion rates at 600 K (▲), 626 K (□), and 658 K (◆).

Table 5
BET surface area of the synthesized pure phases and of the phase mixtures before and after catalytic test

Compound	Surface area ($m^2\ g^{-1}$)
M1(Te)	8.4
M2(Te)	0.4
M1(Nb/Te) + *M2*(Te)[a] before test	4.3 (4.4)[b]
M1(Nb/Te) + *M2*(Te) after test	4.5

[a] *M1*(Nb/Te) + *M2*(Te) contain 50 wt% of each phase.
[b] Weighted sum of the surface areas of the starting single phase.

3.3. *Characterization of the used catalysts*

Allof the catalysts tested, corresponding either to pure phases or to phase mixtures, showed the same X-ray diffraction pattern as before the test. This observation is in good agreement with our previous studies showing that no phase transformation detectable by X-ray diffraction was observed for *M1* and *M2* phase mixtures after the catalytic test [15,18]. The BET surface areas of the phase mixture were measured before and after catalytic testing (Table 5). First it can be seen that the grinding of the phases did not change the surface areas of the individual phases and that the surface area of the phase mixture after catalytic testing was comparable to that measured before the test.

3.3.1. *High-resolution electron microscopy with EDS analyses*

The study by high-resolution electron microscopy was focused on two mechanical phase mixtures, *M1*(Nb/Te) + *M2*(Sb) and *M1*(Nb/Sb) + *M2*(Te) (50–50 wt%), before and after catalytic testing. The micrographs of the phase mixtures did not reveal any specific particle shape, and the morphology appeared to be the same, according to the micrographs, before and after catalytic testing. No new phase was detected by electron diffraction. These results are in good agreement with those obtained by X-ray diffraction and BET surface area measurements. The analyses by EDS of several particles of the mechanical phase mixtures before and after catalytic testing have been used to calculate the atomic ratios for the two phases in the mixtures. These ratios are presented on Table 6. Before catalytic testing the atomic ratios were in good agreement with those previously determined for the phases in synthesized phase mixtures of the type *M1* + *M2*(Nb/Te) and *M1* + *M2*(Nb/Sb) [18–20]. In the *M1*(Nb/Sb) + *M2*(Te) phase mixture, the atomic ratios did not vary much after catalytic testing, except that tellurium was unambiguously detected in the *M1*(Nb/Sb) analysis. At the same time the observed antimony content of the phase was slightly lower. Such a result, which was systematically obtained, can be explained only by the migration of Te to the *M1*(Nb/Sb) phase surface. In the *M1*(Nb/Te) + *M2*(Sb) phase mixture, the atomic ratios did not vary much after

Table 6
Results of EDS analysis of the *M1*(Sb) + *M2*(Te) and *M1*(Te) + *M2*(Sb) mechanical phase mixture before and after catalytic test. Standard deviations for experimental values are given in parentheses

Catalyst	Atomic ratios				
	V/Mo	Nb/Mo	Sb/Mo	Te/Mo	(Sb + Te)/M[a]
M1(Sb/Nb) + *M2*(Te) phase mixture					
M1(Sb/Nb) before test	0.23 (3)	0.17 (6)	0.13 (4)	–	0.09(3)
M1(Sb/Nb) after test	0.21 (3)	0.15 (6)	0.08 (2)	0.06 (3)	0.10(4)
M2(Te) before test	0.35 (4)	–	–	0.38 (6)	0.28 (4)
M2(Te) after test	0.35 (4)	–	–	0.39 (6)	0.29 (5)
M1(Te/Nb) + *M2*(Sb) phase mixture					
M1(Te/Nb) before test	0.24 (3)	0.12 (6)	–	0.10 (2)	0.07 (1)
M1(Te/Nb) after test	0.25 (4)	0.14 (6)	–	0.10 (2)	0.07 (1)
M2(Sb) before test	0.45 (3)	–	0.35 (2)	–	0.32 (2)
M2(Sb) after test	0.43 (4)	–	0.35 (4)	–	0.31 (4)

[a] M = Mo + V + Nb.

Table 7
Comparison of the surface elementary ratios of the cations in the mechanical mixtures calculated from XPS analysis data before (a) and after catalytic reaction (b)

Compound	Element		Binding energy (eV)	M/Mo	$\mathrm{Mo^{5+}/(M^{5+}+Mo^{6+})}$
M1(Nb/Sb) + *M2*(Te)[a]	Mo $3d^{5/2}$	$\mathrm{Mo^{6+}}$	232.3	1.00	0.40
		$\mathrm{Mo^{5+}}$	231.2		
	V $2p^{3/2}$	$\mathrm{V^{4+}}$	516.2	0.15	
	Te $3d^{5/2}$		576.0	0.13	
	Sb $3d^{3/2}$		540.0	0.22	
	Nb $3d^{5/2}$		206.5	0.13	
M1(Nb/Sb) + *M2*(Te)[b]	Mo $3d^{5/2}$	$\mathrm{Mo^{6+}}$	232.4	1.00	0.35
		$\mathrm{Mo^{5+}}$	231.2		
	V $2p^{3/2}$	$\mathrm{V^{4+}}$	516.3	0.14	
	Te $3d^{5/2}$		576.2	0.28	
	Sb $3d^{3/2}$		540.1	0.28	
	Nb $3d^{5/2}$		206.6	0.11	
M1(Nb/Te) + *M2*(Sb)[a]	Mo $3d^{5/2}$	$\mathrm{Mo^{6+}}$	232.5	1.00	0.12
		$\mathrm{Mo^{5+}}$	231.7		
	V $2p^{3/2}$	$\mathrm{V^{4+}}$	516.7	0.14	
	Te $3d^{5/2}$		576.5	0.13	
	Sb $3d^{3/2}$		539.7	0.11	
	Nb $3d^{5/2}$		206.6	0.14	
M1(Nb/Te) + *M2*(Sb)[b]	Mo $3d^{5/2}$	$\mathrm{Mo^{6+}}$	232.5	1.00	0.14
		$\mathrm{Mo^{5+}}$	234.8		
	V $2p^{3/2}$	$\mathrm{V^{4+}}$	516.4	0.12	
	Te $3d^{5/2}$		576.4	0.09	
	Sb $3d^{3/2}$		539.8	0.08	
	Nb $3d^{5/2}$		206.6	0.17	

catalytic testing, and no migration of Sb to *M1*(Nb/Te) was observed, or of Te from *M1*(Nb/Te) to *M2*(Sb) (Table 6).

3.3.2. *XPS analysis*

XPS was used to characterize the surface of the *M1*(Nb/Sb) + *M2*(Te) and *M1*(Nb/Te) + *M2*(Sb) phase mixtures (50–50 wt%) before and after catalytic testing (Table 7). In each case, Mo, V, Te, Sb, Nb, and O were analyzed. The surface compositions of the phases mixtures were slightly different from those calculated from the EDS analyses. The *M1* phases were not as rich in vanadium at the surface as in the bulk, and an excess of antimony or tellurium was observed. Both phase mixtures contained $\mathrm{Mo^{VI}}$ and $\mathrm{Mo^{V}}$. The larger $\mathrm{Mo^{V}}$ content of *M1*(Nb/Sb) + *M2*(Te) compared with the *M1*(Nb/Te) + *M2*(Sb) phase mixture can be explained by the fact that the *M1*(Nb/Sb) phase contained significantly more $\mathrm{Mo^{V}}$ than the *M2*(Sb) phase in the bulk [26].

We showed that the surface composition of the pure *M1* phases did not vary after catalytic testing for the Sb-containing phase but decreased for the Te-containing phase [23]. We found that the surface compositions of the *M1*(Nb/Sb) + *M2*(Te) and *M1*(Nb/Te) + *M2*(Sb) phase mixtures corresponded before testing approximately to that of the two phases, taking into account their relative weight content and respective surface area (Table 1). After catalytic testing it can be observed that an enrichment in tellurium occurred in the *M1*(Nb/Sb) + *M2*(Te) phase mixture, that was not present or was present in very small amounts in the *M1*(Nb/Te) + *M2*(Sb) phase mixture. Such a feature appeared clearly when the Te/Sb surface ratios of the compounds before and after catalytic testing were compared. The ratio changed from 0.6 to 1.0 in the first case and only from 1.1 to 1.2 in the second case.

4. Discussion

The results for catalytic activity presented in this study confirm that the active and selective phase of the MoVTeNbO catalysts is the *M1* phase, whether it contains Te or Sb, and clearly demonstrate that a synergetic effect takes place between the *M1* and *M2* phases (Fig. 1). The maximum yield was observed for a relative mass ratio of *M1* and *M2* around 55% at 600 K. This maximum moves slightly toward high ratios with temperature (Fig. 2). These results, obtained from tests of mechanical phase mixtures, correlate well with the phase composition of the most efficient patented catalysts when they are tested for ammoxidation or oxidation of propane. It was observed, however, that the synergetic effect was higher with mechanical mixtures than with cosynthesized mixtures, which indicates that the synergetic effect is not just a support effect between the two phases. The synergetic effect between the *M1* and *M2* phases was observed only for mixtures in which the *M2* cocatalytic phase contained Te. This correlates well with previous studies showing that a synergetic effect occurred only for mixtures of phases that were efficient in activating propane molecules with phases containing tellurium [15]. This synergetic effect cannot be explained by a change in the morphology of the sample. Scanning electron microscopy study of the two phases and measurements of their surface areas clearly show no difference in the phases before and after catalysis and, in particular, no wetting of one phase by another, which is likely to occur with molybdates [27]. We have seen that when the phase *M1*(Nb/Te) was tested alone or in mixture with *M2*(Sb), a loss of tellurium at the surface was observed [23] (Table 6). The loss of tellurium of the *M1*(Nb/Te) phase should be related to its reduction from Te^{IV} to Te^{0}, which occurred as a side reaction of the catalytic oxidation of propane. A similar effect has been observed with bismuth at the surface of bismuth molybdates during the propene oxidation reaction [28]. However, it should be recalled that no Te^{0} was observed at the surface of the catalysts by XPS. Such a loss of tellurium was not observed when *M1*(Nb/Te) + *M2*(Te) phase mixtures were studied after catalysis, and, indeed, an increase in the surface tellurium content was even observed. This can be explained by the diffusion of tellurium at the surface of the phases from the *M2*(Te) to the *M1*(Nb/Te) phase surface. A comparison of EDS analyses of the *M1*(Nb/Sb) phase in the *M1*(Nb/Sb) + *M2*(Te) phase mixture conducted before and after catalytic testing confirms the migration of Te from one phase to the other. It is difficult to determine from EDS and XPS whether the presence of Te at the surface of the *M1*(Nb/Sb) phase correlates with a decrease in Sb content. The *M2*(Te) phase does not show any loss of tellurium during catalytic testing, but it is inactive.

The first question that may arise is whether the first attribution of the synergetic effect to a bifunctional catalysis with the *M2* phase, selectively oxidizing the propene formed on the *M1* phase, has still to be considered. The results obtained for the antimony-containing catalysts always fits with this interpretation, since the catalytic test of *M1*(Nb/Sb) + *M2*(Sb) did not show any synergetic effect, and the *M2*(Sb) phase was not selective for transforming propene into acrylic acid. It can be observed that the *M1*(Nb/Te) + *M2*(Sb) phase mixture was more selective for acetic acid than was the *M1*(Nb/Te) phase alone. Furthermore, such a feature seems to be relative to the presence of antimony, since all of the phases containing antimony were more selective for producing acetic acid from propane or propene. Since we know that there was almost no tellurium diffusion from one phase to the other, this can be explained only by the transformation of propene formed on the *M1*(Nb/Te) phase by the *M2*(Sb) phase, which was selective for acetic acid (Table 4). This clearly shows that the cause of synergy, earlier described as the oxidative dehydrogenation of the propane molecules on the *M1* phase and the subsequent oxidation of propene on the *M2* phase, has to be taken into account, although it may be markedly less important than the synergy related to the diffusion of tellurium. Furthermore, the fact that the presence or absence of Nb in the *M2* phase has only a slight influence on the selectivity of the phase mixtures, whereas it had been shown to be determinant when tested in the oxidation of propene [24], tends to confirm that the subsequent oxidation of propene on *M2* is not the predominant cause of synergy. Finally, the fact that the formation of acetic acid depends on whether the catalyst contains Sb or Te and is observed to be produced from either propane or propene confirmed that the elements cited are involved in the step corresponding to the oxidation of propene to either acrolein or acetic acid via acetone, as proposed earlier [29].

The second question that may arise is how Te that migrates on the active *M1*(Nb/Te) phase intervenes to increase the selectivity for acrylic acid. It has been shown that the catalyst had a tendency to lose Te during catalysis because of its volatility in the temperature range concerned. Te that migrates would thus replace the lost Te initially present in the hexagonal channel of the active phase structure. The loss of tellurium occurs preferentially at high conversion rates and explains why the synergetic effect is better observed under the latter conditions. It is worth noting that the increase in acrylic acid selectivity observed was mainly dependent on occurring in CO_x. When propene is formed on the catalytic active site, the absence of a Te site, allowing its dehydrogenation and subsequent oxidation to acrolein or acrylic acid, may lead to its total oxidation. It is also possible that Te that had migrated also occupied the heptagonal sites of the active phase. In that case it would create new sites of propene oxydehydrogenation and maybe suppress sites responsible for total oxidation. P. de Santo et al. suggested recently that the effective diameter of the heptagonal channels was comparable to that found in the zeolites LTA and ZSM-5 used for propane separation and cracking and that they may, when unoccupied, trap propane and facilitate the formation of combustion products [30]. It is difficult to propose, from the results of the characterization of the catalysts after catalytic testing, one or the other localization. The fact that the selectivity observed for the *M1*(Nb/Sb) + *M2*(Te) phases mixture corresponds well with that of the pure *M1*(Nb/Te) and that the change in selectivity of the phase mixture, when compared with that of *M1*(Nb/Sb), depends on that in acetic acid and not that in CO_x, indicates migration in the hexagonal channel in place of the Sb sites. However, it seems more probable that tellurium migrates on both types of sites. Finally it has to be noted that the diffusion of tellurium from the *M2* phase to the *M1* phase should depend not only on the ratio of the two phases, but also on their relative surface areas allowing the best contacts. This is indeed what has been observed by Holmberg et al. [16], who stressed that almost no synergetic effect was observed when very large particles of the two phases were mixed.

5. Conclusion

The results obtained in this study clearly confirm that a synergetic effect exists between the two phases *M1* and *M2* of the MoVTeNbO catalysts for the oxidation of propane. This synergetic effect is not observed when the active *M1* phase contains antimony instead of tellurium. The results show that this synergetic effect can be reproduced and amplified simply by mechanical mixing of the powders of the *M1* and *M2* phases prepared independently. The synergetic effect could have two origins: (i) the participation of the *M2* phase in the selective transformation of the propene formed on the *M1* phase into acrylic acid and (ii) the migration of tellurium of the *M2* phase to the surface of the active *M1* phase. The *M1* phase has been shown to lose tellurium. The second cause seems to be major compared with the first one. The best phase ratio for the higher catalytic activities and selectivities depends slightly on the reaction temperature. It is around 55–60 wt% of *M2* at 658 K. However, since one of the major causes of the synergetic effect is related to the diffusion of tellurium from the *M2* phase to the *M1* phase, this phase ratio should depend on the relative surface areas of the two phases allowing the best contacts. The question that remains to be asked is, where exactly is the tellurium coming from the *M2* phase located on the active (0 0 1) plane? It may be that it occupies the hexagonal channel sites liberated by the volatilized tellurium or the empty heptagonal ones or even that it is randomly spread over the surface.

References

[1] R.G. Teller, J.F. Brazdil, R.K. Grasselli, J. Chem. Soc. Farad. Trans. 81 (1985) 1693.
[2] Y. Moro-oka, D.H. He, W. Ueda, in: Symposium on Structure–Activity Relationships in Heterogeneous Catalysis, Meeting, April 22–27, Am. Chem. Soc., Boston, 1990, p. 41.
[3] R.K. Grasselli, Top. Catal. 21 (2002) 79.
[4] P. Ruiz, B. Delmon, Catal. Today 3 (1988) 199.
[5] B. Delmon, G.F. Froment, Catal. Rev. Sci. Eng. 39 (1996) 69.
[6] R.K. Grasselli, Top. Catal. 15 (2001) 93.
[7] J.F. Brazdil, M. Mehicic, L.C. Glaeser, M.A.S. Hazle, R.K. Grasselli, in: M.L. Deviney, J.L. Gland (Eds.), ACS Symposium Series, vol. 288, American Chemical Society, Washington, DC, 1985, p. 26.
[8] H. Ponceblanc, J.M.M. Millet, J.C. Vedrine, in: T. Oyama, G. Hightower (Eds.), ACS Symposium Series, vol. 523, American Chemical Society, Washington, DC, 1993, p. 262.
[9] T. Ushikubo, K. Oshima, A. Kayou, M. Vaarkamp, M. Hatano, J. Catal. 169 (1997) 394.
[10] M. Hatano, A. Kayou, US Patent 5,049,692 (1991), assigned to Mitsubishi chemical Co.
[11] T. Ushikubo, K. Oshima, A. Kayou, M. Hatano, in: C. Li, Q. Xin (Eds.), Stud. Surf. Sci. Catal., Elsevier, Amsterdam, 1997, p. 473.
[12] T. Ushikubo, H. Nakomura, Y. Koyasu, S. Wajiki, US Patent 5,380,933 (1995), assigned to Mitsubishi chemical Co.
[13] P. Botella, E. Garcia-Gonzalez, A. Dejoz, J.M. Lopez Nieto, M.I. Vazquez, J. Gonzalez-Calbet, J. Catal. 225 (2004) 428.
[14] W. Ueda, K. Oshihara, D. Vitry, T. Hisano, Y. Kayashima, Catal. Surv. Jpn. 6 (2002) 33.
[15] M. Baca, A. Pigamo, J.L. Dubois, J.M.M. Millet, Top. Catal. 23 (2003) 39.
[16] J. Holmberg, R.K. Grasselli, A. Andersson, Appl. Catal. A 270 (2005) 121.
[17] R.K. Grasselli, J.D. Burrington, D.J. Buttrey, P. De Santro Jr., C.G. Lugmair, A.F. Volpe Jr., T. Weingand, Top. Catal. 23 (2003) 5.
[18] J.M.M. Millet, H. Roussel, A. Pigamo, J.L. Dubois, J.C. Jumas, Appl. Catal. 232 (2002) 77.
[19] J.L. Dubois, S. Serreau, J. Jacquel, Patent 2 833 005 Fr (2001), assigned to Atofina.
[20] J.L. Dubois, S. Serreau, French Patent FR2844263 (2002), assigned to Atofina.
[21] J.M.M. Millet, M. Baca, A. Pigamo, D. Vitry, W. Ueda, J.L. Dubois, Appl. Catal. A 244 (2003) 359.
[22] J.C. Védrine, Y. Jugnet, in: B. Imelik, J.C. Védrine (Eds.), Les techniques physiques d'étude des catalyseurs, Technip, Paris, 1988, p. 365, Chap. 10.
[23] M. Baca, Ph.D. Thesis, Université Claude-Bernard Lyon 1, 2004.
[24] P. Botella, J.M. Lopez-Nieto, B. Solsona, Catal. Lett. 78 (2002) 383.
[25] F. Borgmeier, A. Tenten, H. Hibst, K. Müller-Engel, S. Unverricht, WO 02/06199A2 (2001), assigned to BASF.
[26] M. Baca, J.M.M. Millet, Appl. Catal. A 279 (2005) 67.
[27] J.M.M. Millet, H. Ponceblanc, G. Coudurier, J.M. Herrmann, J.C. Védrine, J. Catal. 142 (1993) 381.
[28] A. Ayame, K. Uchida, I. Kiyotaka, M. Masazumi, M. Miyamoto, Appl. Catal. A 227 (2002) 7.
[29] E.K. Novakova, J.C. Vedrine, E.G. Derouane, J. Catal. 211 (2002) 226.
[30] P. de Santo, D.J. Buttrey, J. Douglas, R.K. Grasselli, in: Abstracts of Papers, 228th ACS National Meeting, Philadelphia, PA, United States, August 22–26, 2004.