Journal of Catalysis 261 (2009) 166–176

Contents lists available at ScienceDirect

Journal of Catalysis

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Study of Te and V as counter-cations in Keggin type phosphomolybdic polyoxometalate catalysts for isobutane oxidation

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ARTICLE INFO

Article history:
Received 22 July 2008
Revised 12 November 2008
Accepted 12 November 2008
Available online 11 December 2008

Keywords:
Isobutane oxidation
Polyoxometalates catalyst
Heteropolyacid
Methacrylic acid
Vanadyl and tellurium countercation

ABSTRACT

Keggin-type phosphomolybdic acid and cesium salts with protons partially substituted by tellurium and by both tellurium and vanadium have been prepared, characterized using several techniques and tested as catalysts in the partial oxidation of isobutane into methacrylic acid (MAA). The results showed that tellurium when introduced as counter-cation was present as Te^{4+} capping the Keggin anion and was randomly distributed in the acid or in the cesium salt. This cation induced a positive effect on the selectivity to MAA and methacrolein (MA) without significant effect on the activity except in the acid at low loading where it also increased the activity. The co-substitution of protons by vanadyl cations had a slight effect on the selectivity but increased the activity especially at low level of substitution, which led to a very efficient catalyst. Selectivity to MAA and MA and isobutane conversion rate of 65 and 17% respectively were reached at 350 °C and were both very constant with time on stream. The catalytic results obtained in both stationary and transient conditions allowed to propose a reaction mechanism very close to one already proposed with four intermediates amongst which one is common to both MAA and MA. These results were used to understand the catalytic effect of tellurium and vanadium.

1. Introduction

Selective oxidations of light alkanes or olefins can be considered as processes consisting of several successive steps corresponding either to dehydrogenation of the organic molecule or oxygen insertion. Such complex reactions are generally achieved using multicomponent catalysts, with different catalytic sites able to carry out all these steps. The different reaction steps can also be achieved on sites of different phases that cooperate, enhancing the catalytic performances with respect to each component phase and leading to the well-known synergetic effect [1,2]. However, having each reaction step occurring on catalytic sites at the surface of the same phase is preferred. This is particular true for isobutane oxidation reaction to methacrylic acid for which it has been proposed that no or few intermediate compounds that are susceptible to desorb and be selectively further transformed on another phase are formed [3].

Polyoxometalates, which are the best catalysts for this reaction, have the unique ability to undertake partial substitution in the anionic structure as well as in cationic position [4,5]. This allows generating different catalytic sites on the same compound and to tune the acidic and redox properties of these sites to optimize their catalytic properties.

This has been used to design very efficient catalysts for isobutane partial oxidation most of them being molybdenum-based heteropolyacids with Keggin structure and a complex formula that encompasses partial substitutions of the central (As to P) or addenda atoms (V to Mo) in the anion and several metallic counter-cations [6–10]. The individual effect of these substituting elements is not clearly understood and the catalysts obtained while being efficient enough for an industrial application, lack stability.

In this work, we have undertaken the rational design of a new catalyst formula based on the effect of the partial substitution of protons in either pure phosphomolybdic heteropolyacid or mixed protons and cesium salt, by tellurium and vanadium cations. Tellurium was selected for its hydrogen abstracting efficiency reported in the literature on oxidation catalysts [11]. Vanadium cations when substituting Mo cations in the Keggin structure were shown to lead to more efficient catalysts [12–14]. However, vanadium substituted phosphomolybdic anions are not stable over long-term use at the catalytic reaction temperature and a restructuring of the compound with the diffusion of vanadium in countercationic position and a partial destruction of the anions occurs and is detrimental to the catalytic properties [12,15]. Consequently we chose to prepare compounds with pure phosphomolybdic an-

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doi:10.1016/j.jcat.2008.11.013

ions and introduce directly the vanadium in counter-cationic positions.

2. Experimental

2.1. Preparation of the catalysts

The prepared compounds corresponded to pure Keggin-type phosphomolybdic acids or salts. They are all constituted of ($PMo_{12}O_{40}$) anions with protons, Cs, VO and Te as counter-cations and designated according to their metal counter-cation content. For example, $Cs_2Te_{0.2}$ denotes a solid with the stoichiometry $Cs_2Te_{0.2}H_xPMo_{12}O_{40}$, x depending of the reduction level of molybdenum cations. H_xTe_y, $(NH_4)_1Te_1$, Cs_2Te_x and $Cs_2Te_xV_y$ compounds have been prepared. The tellurium containing phosphomolybdic acid samples have been synthesized using a method described for the pure acid [16]. 5.64 g of MoO_3 were dissolved in 150 mL of hot water. 0.34 g of phosphoric acid and various amounts of tellurium were added to the solution and maintained at 80 °C under reflux for 12 h at 80 °C. The final yellow solution was evaporated under reduced pressure and the solid obtained, dried at 125 °C and calcined under a flow of air at 360 °C for 6 h.

To synthesize tellurium containing cesium salts, 140 mL aqueous solutions of 8.16 g of phosphomolybdic acid (FLUKA 79560) and various amounts of telluric acid were prepared. To this solution, 0.4 mL of a second aqueous solution containing 1.3 g of cesium carbonate was added dropwise and a precipitate was formed. After 1 h under stirring at 80 °C, the solution was dried at reduced pressure and the solid obtained, treated similarly to the phosphomolybdic acid samples [17]. An ammonium salt with tellurium has also been synthesized using a similar protocol except that the precipitate was obtained by adding a 37% chloridric acid solution (5 mL) to a 150 mL aqueous solution of ammonium heptamolybdate (8.27 g), phosphoric acid (0.53 g) and telluric acid (0.89 g). This compound has not been studied as catalyst but used for the characterization of the environment of the tellurium cations in counter-cation position by X-ray absorption spectroscopy (XAS).

The vanadium containing compounds were prepared by maintaining the hydrated acid or cesium salt synthesized as described above for 6 h, at room temperature and under stirring in a solution of toluene containing vanadium acetylacetonate. The phosphomolybdic compounds were not soluble in toluene and an exchange of the protons of the compounds by the vanadium cations took place [18]:

$$V[C_5O_2H_7]_3 + 3H^+ + 6H_2O \rightarrow V^{3+}[H_2O]_6 + 3CH_3COCH_2COCH_3.$$

The solids dried under reduced pressure at 60 °C were not calcined but directly heated under the catalytic reaction flow when tested. The compounds were designated according to their metal counter-cation content.

2.2. Characterization techniques

Chemical analysis was determined by atomic emission for Mo, V, Te, and P, using an induced plasma technique, and for Cs, using an air–acetylene flame. The specific surface areas were determined by the BET method using nitrogen adsorption at −196 °C. The infrared spectra were measured as KBr pellets on a Brücker Vector 22 FTIR spectrometer. Raman spectra were recorded using a LabRam HR spectrometer (Jobin Yvon) equipped with a CCD detector. The exciting line at 514.53 nm of an Ar^+–Kr^+ ion laser (Spectra Physics, Model 2018RM) was focused on the samples using a ×100 objective. The influence of the laser on the heating of samples has been previously investigated and a very limited power of 0.1 mW has been used. The homogeneity of the samples has been checked by performing several analyses for each samples.

Table 1
Parameters used for the Mo 3s and V $2p_{3/2}$ decomposition in the XPS spectra.

Peak	Binding energy (eV)	Line width (eV)	Line shape (GL%)[a]
Mo 3s	510.65 ± 0.1	5.9 ± 0.1	30
V $2p_{3/2}$	517.50 ± 0.15	2.5 ± 0.1	30

[a] GL corresponds to the % of Gaussian in Gaussian–Lorentzian fit.

X-ray diffraction patterns were recorded using a Siemens D5005 diffractometer and Cu$K\alpha$ radiation with 0.02° (2θ) steps over the 3–80° angular range with 1 s counting time per step.

Surface analyses by X-ray photoelectron spectroscopy (XPS) were performed in a Kratos Axis Ultra DLD equipped with a magnetic immersion lens, a hemispherical analyzer and a delay line detector. Experiments was performed using a monochromated Al$K\alpha$ X-ray source, with a pass energy of 20 eV and a spot size aperture of 300 × 700µm with a pressure in the analysis chamber below 5×10^{-8} Pa. XPS spectra of Mo 3d, Mo 3s and V 2p levels were measured at 90° (normal angle with respect to the plane of the surface). A charge neutralizer was used to control charges effects on samples. V $2p_{3/2}$ and Mo 3s peaks have been used to determine the surface V/Mo atomic ratio. Because these peaks were very close to each other, the spectra have been decomposed using parameters for the Mo 3s peak determined with respect to the Mo 3d peak (Table 1).

EXAFS spectra at the Te K-edge of the $(NH_4)_1Te_1$ compound before and after heat treatment have been recorded on the experimental station D44 (LURE-DCI storage ring, Orsay, France) using Si/Li mono-element Eurysis solid-state detector and a Si(111) double crystal monochromator. The acquisitions were performed in the range of 31650–32900 eV. The spectra were analyzed by a standard procedure of data reduction using the IFEFFIT code [19]. For the EXAFS analysis, structural parameters were obtained from least squares fitting in R-space, using amplitude and phase of backscattering as well as mean-free-path taken from FEFF codes [20]. XANES V and Te K-edge spectra of the $Cs_2Te_{0.2}V_{0.2}$ compounds have been recorded before and after catalytic testing. The analyses of V and Te K-edge spectra were based on the observations of the pre-edge and edge positions respectively. For vanadium spectra, a linear relation between the energy position of the pre-peak and the formal oxidation state of vanadium has been observed [21, 22]. It allowed determining the average oxidation state of vanadium in the $Cs_2Te_{0.2}V_{0.2}$ compound by a simple measure of the position of the center of mass of the pre-peak. For the Te spectra, the edge position has been compared to that of reference compounds TeO_2 and $(NH_4)_6TeMo_6O_{24}\cdot 7H_2O$ collected under the same conditions.

2.3. Catalysts testing

The oxidation of isobutane to methacrylic acid was carried out at atmospheric pressure in a dynamic differential micro-reactor containing 1 to 2 g of catalyst. A gas feed $O_2/iBu/H_2O/N_2 = 27/13.5/10/49.5$ kPa was used with a total flow rate equal to 6 $cm^3\,min^{-1}$; the gases at the outlet of the reactor were analyzed on line by gas chromatography using a TCD gas chromatograph with CP-Molsieve 5 Å, Silicaplot and Porapak Q columns. The organic substrates were condensed during the reaction and analyzed off-line using a chromatograph equipped with a FID detector and a CPWAX58/FF column. During the first hours, all the catalysts were undergoing a deactivation and the catalytic data were thus systematically collected after at least 8 h. Methacrolein (MA), methacrylic acid (MAA), acetic acid (AcA), CO, and CO_2 were the five major by-products formed under the reaction conditions used. Traces of acetone and acrylic acid have been detected, but most of the

Table 2
Chemical analyses and BET surface areas of the synthesized solids.

Compound	Atomic ratios				BET surface area ($m^2\,g^{-1}$)
	12Cs/Mo	12V/Mo	12Te/Mo	12P/Mo	
H_3	-	–	–	–	1.2
$H_{1,8}Te_{0,6}$	–	–	0.6	1.2	1.3
H_1Te_1	–	–	1.0	1.2	1.7
$Te_{1.5}$	–	–	1.5	1.3	1.9
$(NH_4)_1Te_1$	–	–	0.9	1.2	–
Cs_2H_1	2.1	–	–	1.3	11.1
$Cs_2Te_{0.05}$	2.2	–	0.07	1.1	14.4 (27.4)[a]
$Cs_2Te_{0.2}$	2.1	–	0.20	1.3	9.2 (20.4)[a]
$Cs_2Te_{0.5}$	2.2	–	0.50	1.1	6.9 (11.7)[a]
$Cs_2Te_{0.2}V_{0.05}$	2.0	0.06	0.24	1.3	8.3
$Cs_2Te_{0.2}V_{0.10}$	2.2	0.12	0.25	1.1	10.7
$Cs_2Te_{0.2}V_{0.20}$	2.1	0.21	0.24	1.3	12.0
$Cs_2Te_{0.3}V_{0.10}$	2.0	0.10	0.31	1.2	11.4

[a] Values in parentheses correspond to surface areas before catalytic test.

time, were not considered in the calculations. The carbon balances were always between 96 and 100%. The analysis of acids was checked by chemical analysis using phenolphthalein as indicator. Liquid NMR analysis of the condensed products has periodically been used to insure that no other products were formed even as traces.

In order to gain information on the reaction mechanism, experiments have been conducted using the method of TAP (Temporal Analysis of Products). Transient pulse experiments were carried out in a commercial TAP-2 reactor system (Mithra Technologies Inc.) [23]. The system was equipped with four high-speed pulse valves, a liquid trapped vacuum system, and a quadrupole mass spectrometer located directly underneath the micro-reactor exit. The reactor is typically loaded with 40 mg of 0.2–0.5-mm-size catalyst in the centre of the reactor between two layers of 0.2–0.3-mm-size quartz. Lean mixtures were simulated by introducing alternatively pulses of isobutane and oxygen or 1:1 water–oxygen mixture, over the bare surface of the catalysts at 360 °C, until steady-state coverage was reached.

3. Results

3.1. Chemical analyses and BET surface area measurements of the catalysts

The chemical analyses data of the prepared samples (salts and acids) are presented in Table 2 with the specific surface area measured after catalytic test. The results of the chemical analyses were in good agreement with the theoretical stoichiometries. The specific surface areas of the acids samples were rather low and increased slightly with the tellurium content. Those of the cesium salts were higher but decreased with the tellurium content. In the case of the cesium salts, the surface areas of several compounds have also been determined before catalytic test. The results obtained showed that a strong decrease of the surface area was observed during catalytic testing. Such sintering effect, which occurred when the catalysts were brought into the reaction conditions has already been observed by several authors [24,25]. It explained the strong decrease of the activity of this type of catalysts, taking place systematically during the first hours on stream. The chemical analyses of the $Cs_2Te_{0.2}$ samples with various amounts of vanadyl cations as counter-cations were in good agreement with the desired stoichiometries. Their specific surface areas measured after catalytic test were comparable, although they slightly increased with the vanadium content. The chemical analysis of several samples has been performed after catalytic testing. They all showed that the chemical composition did not vary under catalytic reaction and more specifically no loss of tellurium was detected.

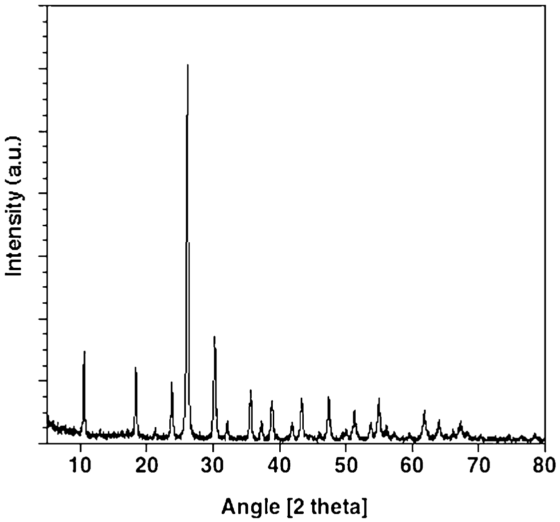


Fig. 1. X-ray diffraction pattern of the compound $Cs_2Te_{0.2}$.

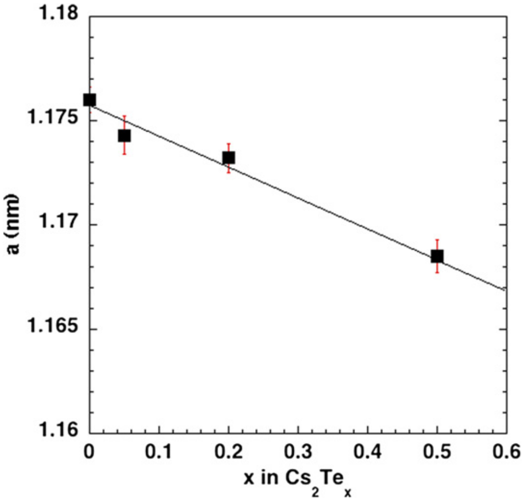


Fig. 2. Variation of the cell parameter of the Cs_2Te_x compounds as a function of the tellurium content.

3.2. X-ray diffraction and XAS spectroscopy characterization of the catalysts

The X-ray diffraction patterns of the tellurium containing acids and cesium salts after heat treatment at 360 °C have been recorded. The diffractograms of the $Cs_2Te_{0.2}$ compound is given in Fig. 1 to illustrate the data obtained. The patterns of the acid samples were similar to those previously reported for the acid phases hydrated at about 8 and 1.5 H_2O [26,27]. The cesium salts patterns exhibited only the cubic phase (Pn3m) commonly associated with the pure alkaline heteropolysalts [28]. The cell parameter of the cubic phase has been calculated for the different cesium salts of the series (Fig. 2). It decreased linearly when the tellurium content increased which tends to show that tellurium was randomly distributed in the cesium salt and that the phase corresponded to a solid solution. The X-ray diffraction patterns of the vanadium containing compounds were similar, exhibiting only the cubic phase with no significant variation of the cell parameter with the vanadium content.

In order to characterize the local environment of Te cations in the heteropolycompounds, a tellurium containing ammonium salt $(NH_4)_1Te_1$ has been prepared and characterized by EXAFS at Te K-edge just after precipitation and after heat treatment. Its X-ray

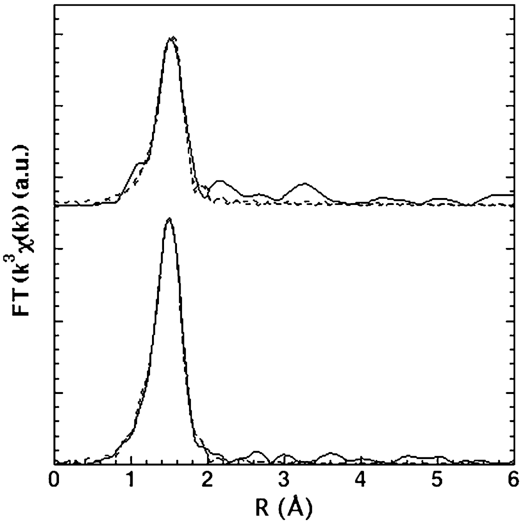


Fig. 3. Magnitudes of Fourier-transformed spectra of the Te K-edge spectra of the compound before (top part) and after (bottom part) heating under air at 360 °C; experimental data full lines and calculated ones dashed lines.

Table 3
Te K-edge EXAFS fit results for the (NH_4)Te compound before and after heat treatment and edge energy calculated from the XANES spectra compared to reference phases.

Compounds	Site	Edge energy (eV)	*R* (Å)	σ^2 (Å^2)	*N*
$(NH_4)_6TeMo_6O_{24}$	Te^{6+}	31,838.3			
(NH_4)Te-25 °C	Te^{6+}	31,838.3	1.92	0.0019	6
TeO_2	Te^{4+}	31,829.6			
$(NH_4)_6$Te-360 °C	Te^{4+}	31,829.2	1.90	0.0040	4

diffraction after heat treatment corresponded to that of a cubic phase and its chemical composition was in agreement with the desired one (Table 2). Fig. 3 shows the modulii of the Fourier transformed spectra of k^3-weighted EXAFS of the solids. A good fit of the first peak was found when considering 6 Te–O distances at 1.92 Å for the solid before heat treatment and 4 Te–O distances at 1.90 Å after heat treatment (Table 3). Before heat treatment, the Te cation should be surrounded by 6 OH groups like in H_6TeO_6 and the observation in the infra-red spectrum besides the bands corresponding to the Keggin heteropolyanion [29] of a band at 668 cm^{-1} attributed to a Te–O–H vibration confirmed this interpretation (data not shown) [30]. It is likely that telluric acid has been precipitated besides the heteropolycompound. Furthermore, the XANES spectrum of the compound showed that tellurium was +6 before heat treatment (Table 3, Fig. 4). After heat treatment, both the oxidation state and the environment of tellurium have changed. Tellurium was present as Te^{4+} cation with 4 close oxygen neighbors forming with the electron lone pair *E* a distorted trigonal bipyramid as in several compounds like crystalline α or βTeO_2 [31]. This was confirmed by the profile of the XANES spectrum obtained with the absence of a shoulder on the high-energy side of the first peak similarly to that simulated for such $[TeO_4]$ clusters with FEFF8 [32]. To exhibit such environment with the metal–oxygen bond determined, Te cation should be capping Keggin anions and be bound to four oxygens of the same Keggin unit. This coordination has already been observed for vanadyl or molybdyl cations when capping the same type of anion [33,34].

The XANES spectra at V K-edge recorded for the $Cs_2Te_{0.2}V_{0.1}$ compounds before and after catalytic testing showed an average oxidation state for vanadium respectively equal to 4 and 4.1 (Fig. 5). This result was compatible with the binding energy attributed to V^{4+} measured by XPS. It may be postulated that vanadium was present in counter-cation position as vanadyl cations capping the Keggin anions as shown previously [34].

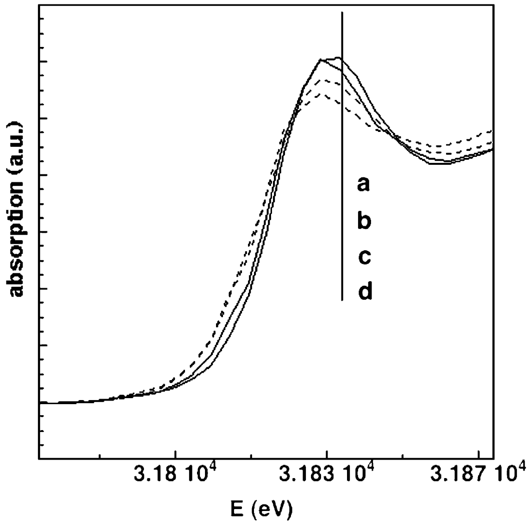


Fig. 4. Te K-edge XANES spectra of the $Cs_2Te_{0.2}V_{0.1}$ compound before (b) and after catalytic test (d) and of reference phases $(NH_4)_6TeMo_6O_{24}$ (a) and TeO_2 (c).

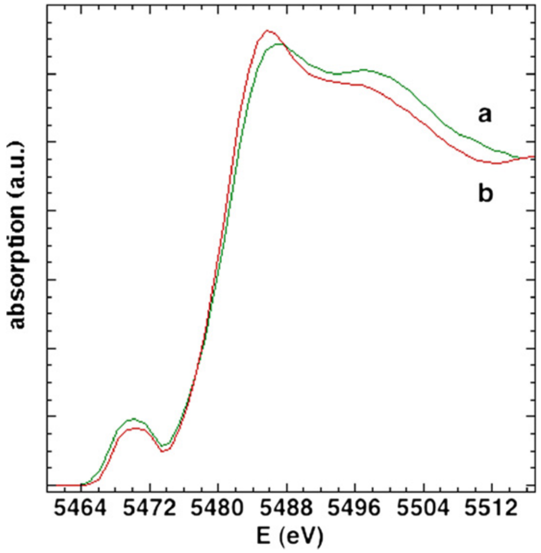


Fig. 5. V K-edge XANES spectra of the $Cs_2Te_{0.2}V_{0.1}$ compound before (a) and after catalytic testing (b).

3.3. XPS and Raman spectroscopy characterization of the catalysts

Raman spectroscopy has been used to characterize the Cs_2Te_x compounds and the $Cs_2Te_{0.2}V_{0.1}$ compound, before and after catalytic testing; the spectra of several compounds are presented in Fig. 6. The spectrum of the Cs_2H_1 compound, which corresponded to that of the cesium Keggin-type phosphomolybdic salt showed few changes before and after catalytic testing [36]. On the contrary, all the tellurium containing compounds exhibited after catalytic testing besides peaks characteristic of the Keggin-type salt, new peaks at 1024, 1008, 844, 790, 732, 676, 628, 545, 495, 306, 283 and 183 cm^{-1} (Table 4). These peaks, which were only weakly visible before catalytic test and more intense after, did not correspond to MoO_3 neither to heteropolyanions fragments as described

Table 4
Raman bands positions in the spectra of the compound $Cs_2Te_{0.2}$ before and after catalytic testing. Assignments of the main bands **1**: ν_s Mo=O$_d$; **2**: ν_{as} Mo=O$_d$; **3**: ν_s P–O; **4**: ν_{as} Mo–O$_b$–Mo.

Compound	Frequencies (cm^{-1})																									
					1	**2**	**3**	**4**																		
$Cs_2Te_{0.2}$av.	1607	1560			990	973	961	880						607			386	348			258	238	229		168	137
$Cs_2Te_{0.2}$ap.	1600	1572	1024	1008	991	974	962	880	844	790	732	676	628	605	545	495	386	348	306	283	258	238	227	183	170	143

Table 5
Results of the XPS analysis of the tellurium and cesium salts analyses before catalytic testing (after calcination at 360 °C) and after catalytic testing at 340 °C in standard conditions.

Catalyst	Element	Binding energy (eV)		Atomic ratios			
		Before testing	After testing	Before testing		After testing	
				M/P	$Mo^{5+}/(Mo^{5+}+Mo^{6+})$	M/P	$Mo^{5+}/(Mo^{5+}+Mo^{6+})$
Cs_2H_1	Cs 3d$_{5/2}$	724.1	724.1	0.97		1.08	
	Mo 3d$_{5/2}$	233.2	232.9				
		231.4	230.9		0.10		0.17
	P 2p	134.2	134.2				
$Cs_2Te_{0.05}$	Cs 3d$_{5/2}$	724.2	723.9	1.33		1.53	
	Te 3d$_{5/2}$	577.7	577.4	0.04		0.08	
	Mo 3d$_{5/2}$	233.3	233.8				
		231.5	232.5		0.03		0.02
	P 2p	134.5	134.3				
$Cs_2Te_{0.2}$	Cs 3d$_{5/2}$	724.2	724.1	2.00		2.00	
	Te 3d$_{5/2}$	577.5	477.4	0.22		0.22	
	Mo 3d$_{5/2}$	233.3	233.8				
		231.2	232.5		0.10		0.05
	P 2p	134.2	134.2				
$Cs_2Te_{0.5}$	Cs 3d$_{5/2}$	724.2	724.0	1.82		2.07	
	Te 3d$_{5/2}$	577.2	577.5	0.46		0.51	
	Mo 3d$_{5/2}$	233.3	233.9				
		231.4	232.6		0.09		0.07
	P 2p	134.2	134.2				

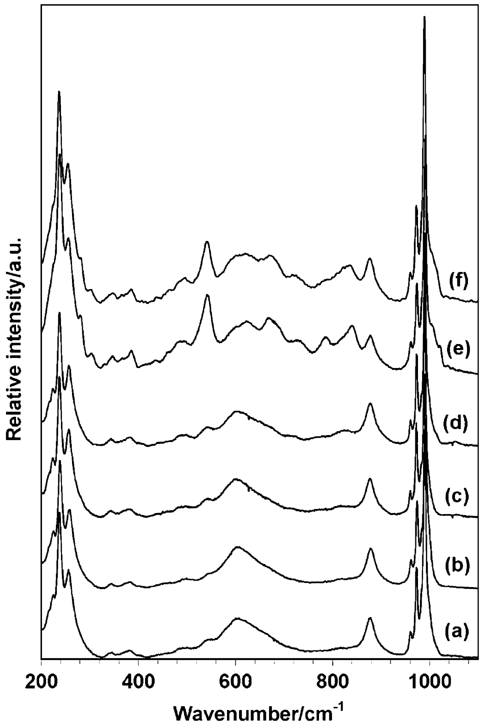


Fig. 6. Raman spectra of the compounds Cs_2H, $Cs_2Te_{0.2}$ and $Cs_2Te_{0.2}V_{0.1}$ before (a, b, c) and after catalytic testing (d, e, f).

by Mestl et al. [15]; these new peaks have been observed for the reference sample $Mo(H_2O)_2(MoO)_2PMo_{12}O_{40}$ and attributed to capped heteropolyanions bonds vibrations [37].

The surface chemical composition of several Cs_2Te_x compounds has been determined by XPS. The results showed that the surface Te and Cs compositions were comparable to the bulk ones (chemical analyses) confirming the formation of solid solutions (Table 5). The molybdenum (Mo 3d$_{5/2}$) peaks could be decomposed into two peaks corresponding to Mo^{5+} and Mo^{6+} species. All the solids appeared reduced at the surface but no relation between the presence of tellurium and the relative ratio of Mo^{5+} could be drawn. After catalytic testing the surface composition as well as the ratio of Mo^{5+} did not really vary and no loss of tellurium was observed. It may be noted that for the catalysts after catalytic testing with a high Te content, the best fits of the Mo signal were obtained with a second Mo^{6+} with a larger binding energy (234.00 eV). These new species, which represented only few % (<6%) of the total Mo species have not been interpreted and are presently under study.

The variation of the surface vanadium content as a function of the bulk vanadium content of the $Cs_2Te_{0.2}V_x$ compounds has been the focus of a specific study. A surface enrichment compared to the bulk was evidenced particularly at low V content (Fig. 7). It could be related to the method of addition of vanadium as countercation, which proceeded through a cationic exchange without dissolution of the cesium and tellurium salt.

3.4. *Isobutane oxidation*

The catalytic results obtained for the synthesized compounds in conventional testing apparatus are presented in Table 6. They showed that the substitution of protons by tellurium in the acid and the cesium salt has a strong positive effect on the selectivity to methacrylic acid (MAA) and methacrolein (MA). In parallel, a small decrease of the activity was observed for the acid and a

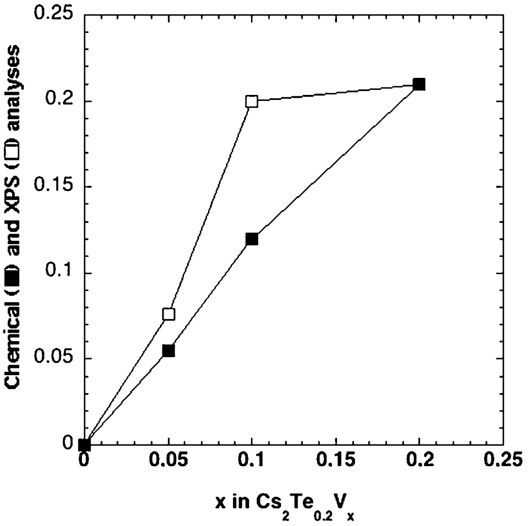


Fig. 7. Bulk and surface composition in vanadium determined from chemical analyses and XPS data.

Table 6
Catalytic properties of Te substituted acid and the phosphomolybdic cesium salt. Testing conditions: contact time 4.8 s, mass of catalyst 2 g, composition of the reaction mixture iBu/O_2/H_2O/N_2 = 27/13.5/10/49.5. AcA: acetic acid, MA: methacrolein, MAA: methacrylic acid.

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)					Yield (%) AMA + MA
			CO	CO_2	AcA	MAA	MA	
H_3	310	1.3	16	45	11	11	16	0.4
	345	3.5	23	44	15	9	9	0.6
	355	4.4	32	34	18	6	10	0.7
$H_{1.8}Te_{0.6}$	310	2.3	11	15	9	27	39	1.5
	330	3.9	14	16	10	25	36	2.4
	355	6.3	19	18	13	27	22	3.1
H_1Te_1	325	2.6	4	7	4	41	43	2.2
	340	3.4	6	10	4	40	40	2.7
	360	4.8	10	13	5	33	39	3.5
$Te_{1.5}$	310	2.2	7	15	4	46	28	1.6
	345	3.4	8	14	6	41	31	2.4
	355	4	11	15	7	37	30	2.7
$Cs_2Te_{0.05}$	324	7	22	23	7	33	15	3.4
	347	9.9	28	21	11	30	10	3.9
	369	14.4	27	23	11	25	13	5.4
$Cs_2Te_{0.2}$	330	7	9	9	5	60	16	5.3
	352	10	13	12	7	55	13	6.8
	367	12	15	13	10	50	12	7.4
$Cs_2Te_{0.5}$	325	5.4	4	6	4	71	13	4.2
	345	7.9	5	7	5	67	16	6.6
	370	10.8	9	10	10	52	19	7.8

small increase for the cesium salt. In the later case the conversion decreased, but since the specific surface area decreased even more significantly, the intrinsic rate of isobutane transformation increased. The substitution of protons by vanadyl cations in the $Cs_2Te_{0.2}$ catalysts increased the conversion with only a slight decrease of the selectivity in MAA and MA (Fig. 8).

The effect of the addition of water to the gas feeds has been studied on the $Cs_2Te_{0.2}$ sample (Fig. 9). Isobutane conversion increased with increasing water pressure up to 10% and then decreased. A positive effect on the selectivity toward MAA and MA was observed. This effect was more pronounced at low water content, which led to an optimal yield in MAA and MA with a water content of 10%. The effect of water has been studied on the vanadium containing catalysts. It appeared to be the same with an optimal yield for the same water content. These results suggest that water influences not only the number or accessibility of the active sites but also these sites intrinsic properties. The decreased conversion observed at high water content could arise from a preferential adsorption of water on these sites.

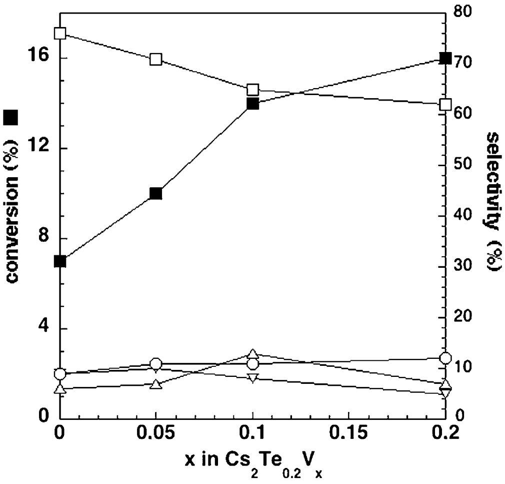


Fig. 8. Variation of isobutane conversion (■) and selectivity to AcA (△), CO (▽), CO_2 (○) and MAA + MA (□) as a function of the vanadium content of the $Cs_2Te_{0.2}$ salt at 335 °C; contact time 4.8 s, catalyst mass 2 g, iBu/O_2/H_2O/N_2 = 27/13.5/10/49.5.

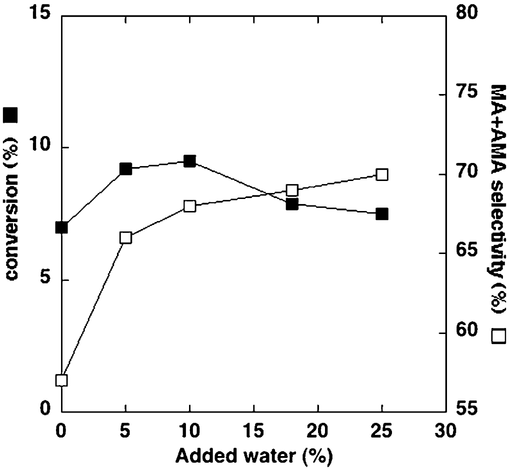


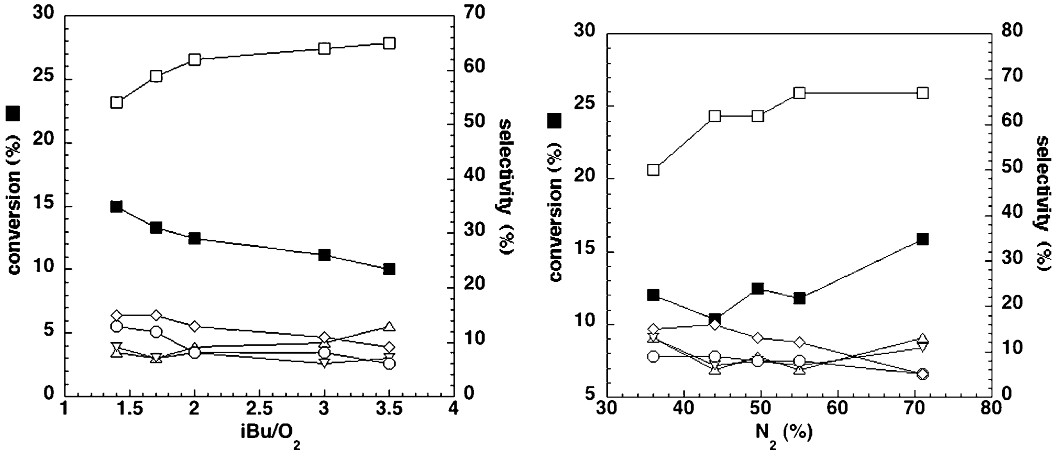
Fig. 9. Effect of addition of water on the isobutane conversion (■) and on the selectivity to methacrolein and methacrylic acid (□) at 330 °C.

Table 7
Catalytic properties of the compound $Cs_2Te_{0.3}V_{0.1}$. Testing conditions: contact time 4.8 s, mass of catalyst 2 g, composition of the reaction mixture: iBu/O_2/H_2O/N_2 = 27/13.5/10/49.5. AcA: acetic acid, MA: methacrolein, MAA: methacrylic acid.

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)					Yield (%) AMA + MA
			CO	CO_2	AcA	MAA	MA	
$Cs_2Te_{0.3}V_{0.1}$	330	10.4	5	9	6	66	14	7.6
	345	14.9	11	13	8	56	12	10.1
	350	16.1	12	14	9	54	11	10.5

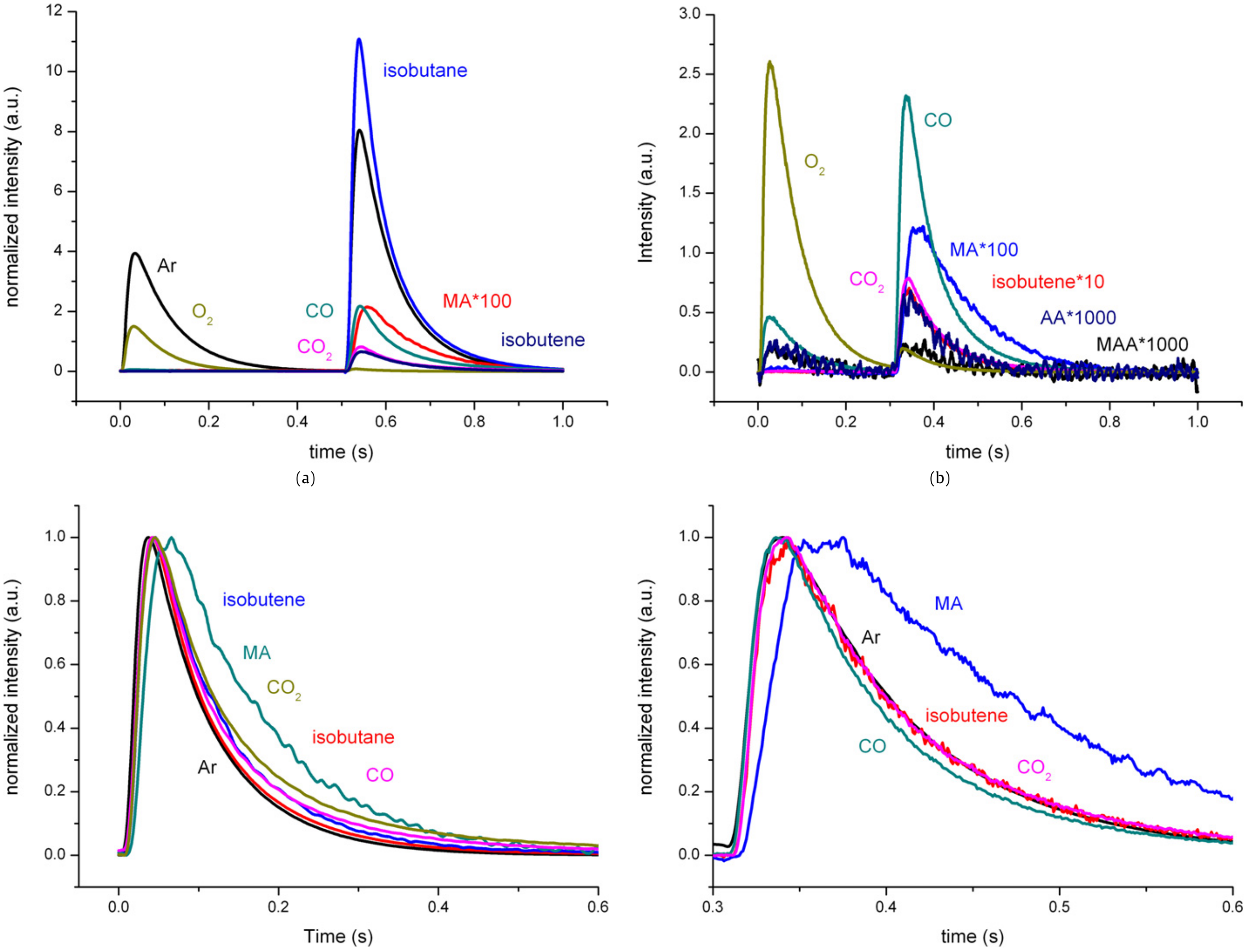
The catalyst composition has been optimized varying concomitantly the vanadium and tellurium contents. The best properties have been obtained for the compound $Cs_2Te_{0.3}V_{0.1}$ (Table 7) [38]. The influence of the gas phase composition in terms of isobutane to oxygen ratio and dilution into nitrogen, has been studied on this catalyst. The results obtained are shown in Fig. 10.

To better understand the reaction mechanism, we have conducted a study using a TAP reactor. We have pulsed alternatively isobutane and O_2 or $O_2 + H_2O$ (in Ar 50%) over a $Cs_2Te_{0.2}$ cata-



(a) (b)

Fig. 10. Schematic representation of the charge composition and evolution of the isobutane conversion (■), selectivity to MAA (▲), MA (◆), AcA (●), CO (○), CO_2 (□) as a function of the i-C_4H_{10}/O_2 ratio (a) and dilution in N_2 (b) on $Cs_2Te_{0.3}V_{0.1}$, at 340 °C in the standard testing conditions.



(a) (b)

(c) (d)

Fig. 11. Mass intensity vs. time curves of desorbing reaction intermediates produced by (a) pulsing successively isobutane and a 1:1 O_2/H_2O mixture (after 0.5 s) over $Cs_2Te_{0.2}$ at 360 °C, (b) pulsing successively isobutane and a 1:1 O_2/H_2O mixture (after 0.5 s) over $Cs_2Te_{0.2}$ at 360 °C; (c) and (d) correspond to the normalized responses, respectively, obtained on isobutane pulses.

lyst at 360 °C. In all cases the observed conversion was rather low, probably due to both the low contact time in the TAP reactor and the low concentration of species adsorbed at the surface of the catalyst. When O_2 was pulsed alternatively with isobutane, only traces of CO_2 were obtained on the O_2 pulse, but CO, CO_2 (major product), water and methacrolein were formed on the isobutane pulse (Fig. 11a). Fig. 11b, where the peak maxima were normalized to facilitate time comparisons, shows the pulse response sequence of the reactants and products: first isobutane, followed by isobutene, then methacrolein and carbon oxides. No methacrylic acid was detected. The peak of carbon dioxide was large, probably because it arised mainly from the subsequent transformation of the adsorbed intermediates into CO_2 on the catalyst surface.

When $O_2 + H_2O$ (1:1 ratio) was pulsed instead of O_2, methacrylic and acetic acids were observed on the isobutane pulse (Figs. 11c and 11d). These results showed that the acids were strongly adsorbed at the surface and that water was a key parameter in their desorption. The products always came out in the order "isobutane, isobutene, methacrolein and CO_2." When the acids were formed, their signals came after that of methacrolein although some acid appeared at the beginning of the pulse. This observation led us to postulate that a certain amount of acid was already present on the surface before the adsorption and was simply displaced by the later.

4. Discussion

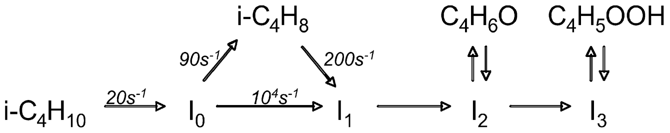
The characterization of the phosphomolybdic acid and cesium salt with tellurium and vanadium as counter-cations showed that the later elements were present as Te^{4+} and $(VO)^{2+}$ cations capping the phosphomolybdic Keggin unit. Tellurium was randomly distributed in the acid and the cesium salt whereas en enrichment in vanadium was observed at the surface. The tellurite entities corresponded thus to TeO_4E with one lone electron pair (E) stereochemically active and credibly oriented in opposition to the four oxygen of the Keggin unit similarly to the oxygen of the vanadyl species. To balance charges in the capped anions, molybdenum cations have to be reduced. It was not possible to determine the extent of reduction of Mo in the capped anions neither whether the anions are single or bi-capped as it has been shown to be possible in several compounds [33,34]. In the Cs_2Te_x compounds, XPS analyses showed a reduction of molybdenum corresponding approximately to 5 Mo^{5+} per Te cation except at high Te content where it is lower.

This could be consistent if single or bi-capped anions are considered, with respective formula of the type $[PMo_4^{5+}Mo_8^{6+}O_{40}\text{-}Te^{4+}]^{3-}$ or $[PMo_8^{5+}Mo_4^{6+}O_{40}Te_2^{4+}]^{3-}$. At high Te content all Te cations may not be capping the heteropolyanions, which would explain the lower reduction rate of Mo observed by XPS. With addition of vanadium, $[PMo_6^{5+}Mo_6^{6+}O_{40}(VO^{2+})_2]^{5-}$ polyanions could be formed as reported previously [35]. In compounds with or without cesium, protons would balance anions charges. Complementary characterization have presently been undertaken in order to determine the oxidation state of molybdenum cations and the exact structure of the anions.

The results of the isobutane oxidation over the studied compounds revealed that either in the acid form or as the cesium salt, tellurium has a strong positive effect on the selectivity to MAA and MA whereas vanadium has an effect on the activity.

The nature of the real pathway in the oxidation of isobutane into methacrylic acid has been extensively debated but controversies still remain. Several authors proposed the intermediate formation of isobutene [10,39,40] while others assumed a direct formation of methacrolein [2,4,41,42]. Among the latter, some authors although they do not include isobutene in the reaction network, do not exclude its formation but with a rapid further oxidation [2,4]. We did not detect any isobutene in our conventional testing experiments, like in most of the experiments of the same type reported in the literature, but our TAP experiments clearly showed that isobutene was first formed and should be considered as an intermediate. Two reasons may explain why isobutene was not observed in conventional testing experiments. First isobutene is oxidized much faster than isobutane. Schindler et al. who have studied the oxidation of isobutane and isobutene on the same catalyst report that isobutene is oxidized about 500 times faster than it is formed via isobutane [10]. Secondly the catalytic oxidation of isobutene did not take place just at the surface of the polyoxometalates catalysts but a significant number of surface layers participated to the reaction. This was clearly shown when the oxidation of isobutene was studied by DRIFT on this type of compounds (data not shown). This feature increases the probability for isobutene molecules to be oxidized before reaching and leaving the surface.

The pathway proposed with two main adsorbed intermediates corresponding respectively to an alkoxide and a dioxyalkyldiene appears to be a good working model and this proposal was taken as the basis [4]. However we propose a slightly different and more complete pathway with the existence of other adsorbed intermediates, which can lead to isobutene and to MAA and MA as shown in the following scheme,



and in Fig. 12. The pulse responses of isobutane, isobutene and methacrolein (MA) obtained from TAP experiments have been modeled according to the scheme (Fig. 13). This scheme contains two parallel routes, one through surface intermediates, the second through the formation of gas phase isobutene. The oxidation of MA has not been taken into account in the modeling and therefore the predicted MA response is much broader than the experimental one. The values of the apparent rate constants for the different steps are reported in the same scheme. The low conversion leads to rather large errors on the individual rate constants, but the relative rates still give a good indication on the different reaction routes. The ratio of the values for the surface reaction of I_0 to I_1 to the desorption rate of I_0 into isobutene amounts to 100, thus favoring a surface route rather than the gas phase route. This explained that isobutene was not observed in steady-state experiments but completely converted due to the significant longer contact times than in the TAP reactor. The ratio of 10 between the adsorption of isobutane to the adsorption of isobutene explains the much higher reactivity for isobutene. This ratio was however lower than what was observed by Schindler et al., probably due to the very different conditions in the TAP reactor.

The intermediate I_2, which is common to both methacrylic acid and methacrolein would undergo either a dissociation of a C–O bond leading to methacrolein or an hydration followed by a subsequent dehydrogenation to form methacrylic acid as shown in Fig. 12. Water in such case would not only help to the desorption of the reactions products but also be involved in the reaction mechanism. This could add an explanation to the positive role of water both on the activity and the selectivity of the catalysts. The results of the TAP experiments however tend to show that its main role is the first one since the observations of methacrylic and acetic acid in the products both completely depend upon the addition of water in the pulse.

In view of the results of the catalyst testing study, the role of tellurium may be clarified. The variation of selectivity to MA has been plotted as a function of the selectivity to MAA for all the acids and the cesium salts tested (Fig. 14). Over the cesium salts, upon increasing Te content the selectivity to MAA alone increased. Over the acids, the same feature was observed at high Te content but at low content the selectivity to MA also increased. This led to propose that the main role of Te was to favor the transformation of the I_2 intermediate into MAA. This would explain the large increase in MAA selectivity. The effect is all the more visible as methacrylic acid is quite stable and acetic acid and carbon oxides

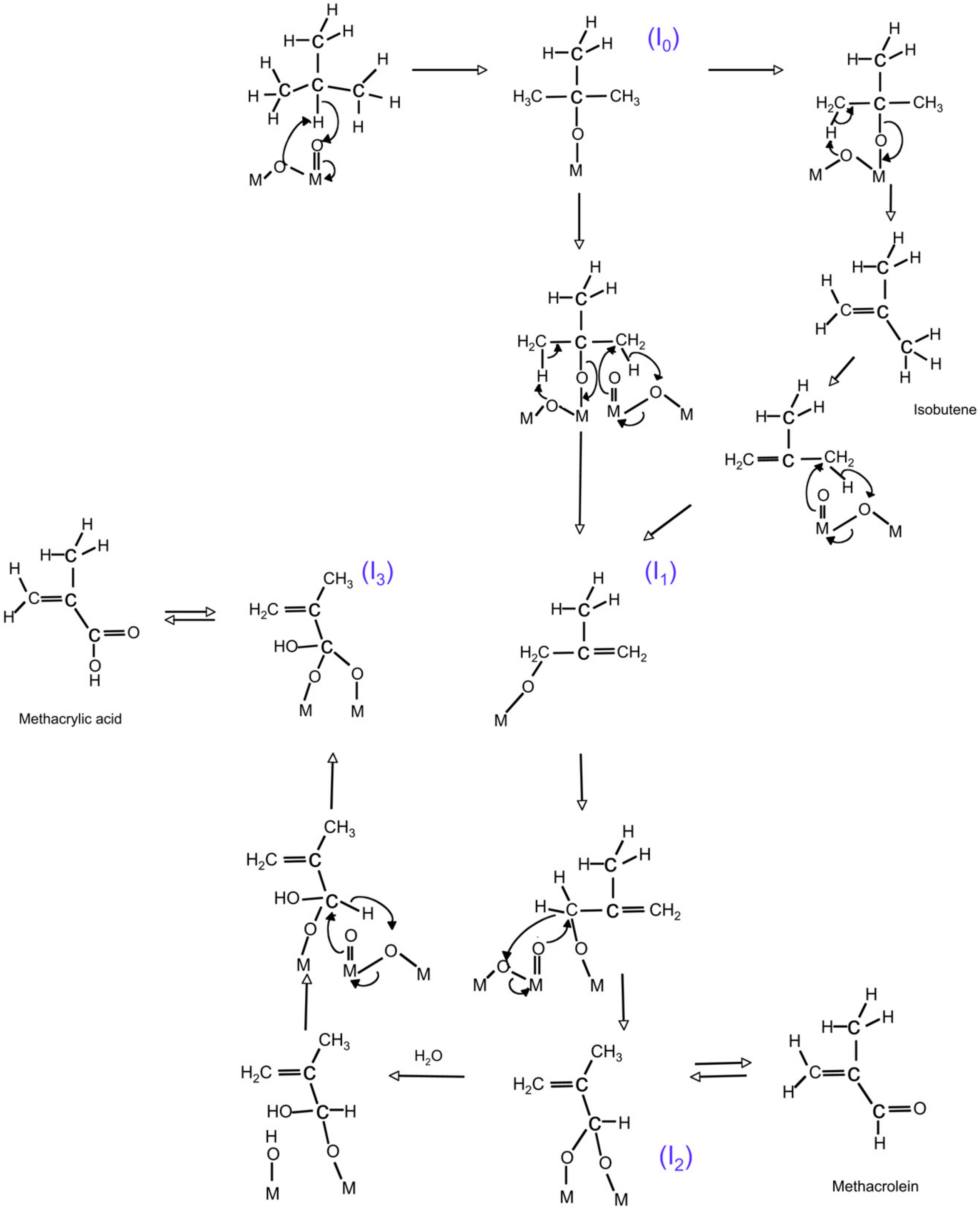


Fig. 12. Proposed mechanism for isobutane oxidation; the degradation reactions of MAA, MA, isobutene or intermediates have not been schematized.

are mainly formed from the oxidative degradation of methacrolein. Te^{4+} should intervene in the dehydrogenation step, because of its hydrogen abstracting efficiency already reported in many oxidation reaction of alkenes and alkanes and common to elements possessing a lone pair of electrons like Bi^{3+} or Sb^{3+} [1,2]. However it cannot be excluded that it also played a role in the hydration step. In the case of the acid, at low content, Te should also help the transformation of the I_1intermediate into I_2. This transformation implies dehydrogenation steps that Te could promote.

The effect of vanadium was less easy to be interpreted from the results. The isobutane conversion increased almost linearly with the vanadium content (Fig. 8) but when the intrinsic rate of isobutane transformation is plotted as a function of the vanadium content, an increase was observed at low V content but not at high;

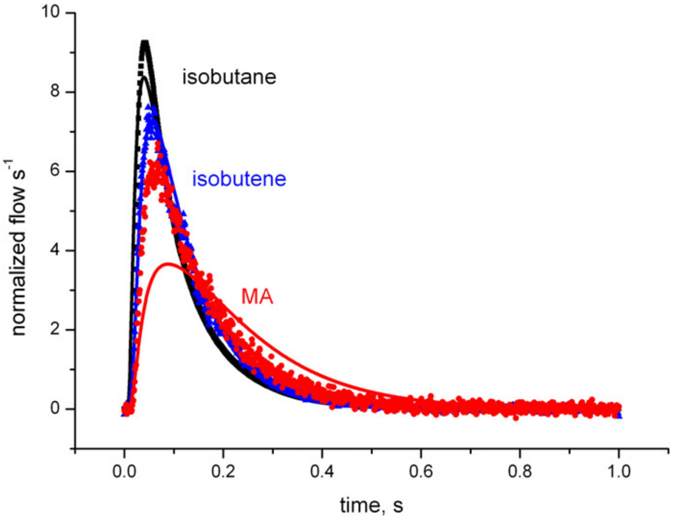
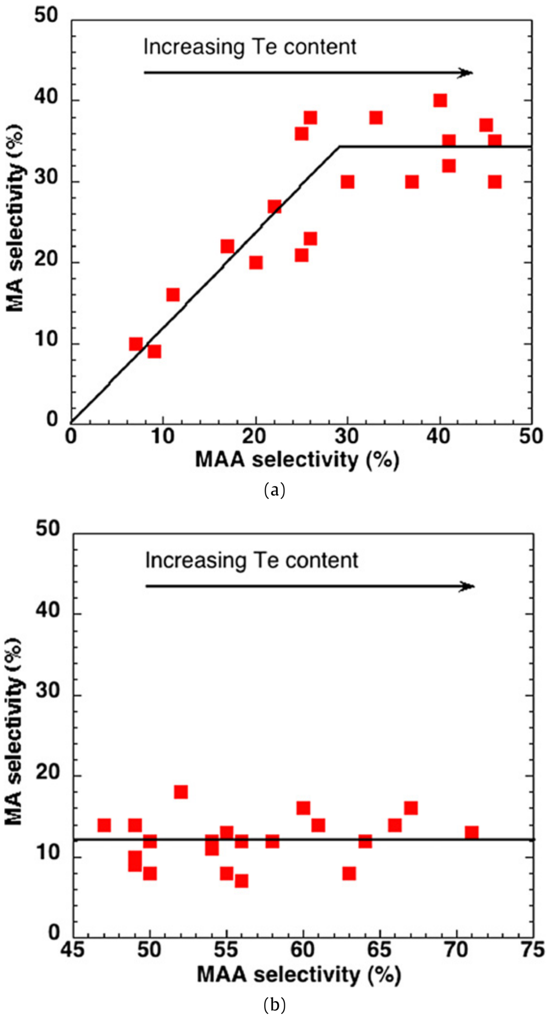


Fig. 13. Experimental (symbols) and calculated (lines) pulse responses of isobutane, isobutene and methacrolein over the $Cs_2Te_{0.2}$ catalyst at 360 °C.



(a)

(b)

Fig. 14. Variation of the selectivity in methacrylic acid (MAA) as a function of that in methacrolein (MA) on the different Te containing acids H_xTe_y (a) and cesium salts $Cs_2Te_xV_y$ (b) studied.

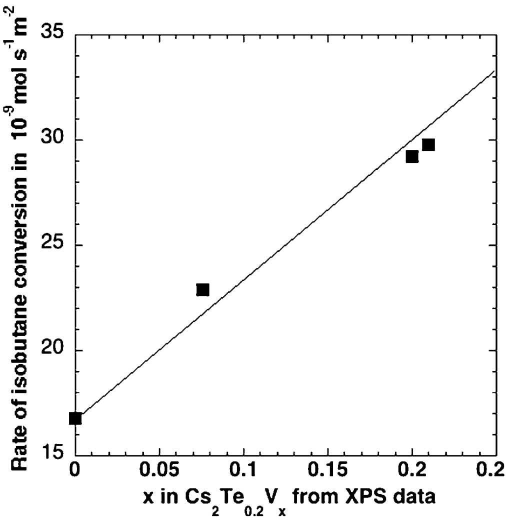


Fig. 15. Variation of the rate of transformation of isobutane as a function of the surface vanadium content of the $Cs_2Te_{0.2}V_x$ compounds determined by XPS.

this shows that the increase in activity could be partially related to the increase of the specific surface area of the compounds but that there was also a modification of catalytic sites. This can be evidenced when the evolution of the V surface composition determined by XPS is plotted as a function of the bulk composition (Fig. 15). The V surface composition was shown to follow the same evolution that the intrinsic rate. The surface enrichment detected at low V content, could be related to the method of addition of V as counter-cation, which proceeded through a cationic exchange without dissolution of the cesium and tellurium salt. It might be postulated that new more efficient sites were formed when vanadium was present. Such hypothesis is supported by the fact that a change of the apparent activation energy for the transformation of isobutane was systematically observed for the V containing cesium salts (76 ± 2 instead of 82 ± 2 kJ/mol).

Finally, it is rather difficult to compare the catalytic properties of our catalysts to those patented or published since turnover frequencies or intrinsic rates of isobutane conversion are never given. The only comparison that could be made is a comparison of productivity in MAA + MA produced per gram of catalyst and per hour. Based upon this number, the catalysts described in this paper, reached productivity between 0.85 and 0.9, which is superior to many of the patented catalysts and close to the best one with around 1.0 obtained at the same total pressure and temperature [43]. These results are quite encouraging, as the preparation of the catalysts can still be improved and defined and because of the fact that the catalysts were very stable with time on stream. This stability, which is a very positive attribute for a possible industrialization, may be due to a higher stability of the heteropolyanions in relation with their purely molybdic composition or to their capping.

5. Conclusion

The results presented in this paper showed that the substitution of protons by Te in phosphomolybdic heteropolyacid and cesium salt was possible. The characterization of obtained compounds showed that after dehydration, Te cations capped the Keggin anions similar as molybdyl and vanadyl cations. They have a strong effect on the selectivity to MAA of both the Keggin phosphomolybdic acid and its cesium salt. In the case of the pure acid they have also a positive effect on the selectivity to MA. Such effect may be attributed to their hydrogen abstracting efficiency already reported in the literature in other oxidation reactions. The concomitant substitution of protons by vanadyl cations allowed increasing the activity of the catalysts without loosing too much selectivity to MAA and MA. The catalyst composition has been optimized and corresponds according to the characterization results to the formula $Cs_2Te_{0.3}(VO)_{0.1}$. The reduction level of the phosphomolybdic anions and the residual protons content has still to be determined. The catalyst has an efficiency comparable to numerous patented catalysts of the same type with a simpler formulation and most of all a very good stability. A reaction pathway relatively similar to one already published has been proposed. It takes into account the formation of isobutene, which was clearly demonstrated from TAP experiments.

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