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Role of acid and redox properties on propane oxidative dehydrogenation over polyoxometallates

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Abstract

$Cs_{2.5}H_{1.5}PV_1Mo_{11}O_{40}$ heteropolyoxometallate compounds have been studied for propane oxidative dehydrogenation (ODH) in the 340–400 °C temperature range. Their redox and Brønsted acid properties have been tuned by introducing a redox metal element M such as Co^{II}, Fe^{III}, Ga^{III}, Ni^{II}, Sb^{III} or Zn^{II} in a V:M atom ratio equal to 1:1. This introduction was carried out either directly in the synthesis solution or by usual aqueous cationic exchange of protons of the solid Cs salt. TGA and FT-IR analyses allowed us to determine the extent of metal M substitution for Mo^{VI} in the Keggin anion and proton replacement by the M cation. It was observed that, under catalytic conditions (C_3:O_2:He = 2:1:2, flow rate 15 $cm^3\,min^{-1}$, 12 h on stream), the catalysts were stable, with only a small part of the substituted elements (V and/or M) being extracted from the Keggin anion during the reaction. The presence of these metal M cations enabled us to tune the redox and acid properties of the material and to get high selectivity for propene (60–80% at 5 and 10% propane conversion) at a relatively low temperature (300–400 °C). The direct synthesis method was found more efficient than the classical cationic exchange technique for propane ODH.

Keywords: Propane ODH; Acid/redox properties; Redox metals: Co, Ni, Fe, Ga, Sb, Zn; Keggin heteropoly compounds

1. Introduction

The catalytic selective oxidation of light parafins to olefins or oxygenates is a potentially important process to utilise alkane feed. Propane selective oxidative dehydrogenation (ODH) to propene or selective oxidation to acrolein or acrylic acid have been extensively studied in the last 20 years both in academia and in industry. For the ODH reaction vanadium appears to be the most crucial element, for instance for catalysts such as VMgO [1,2] or V_2O_5 on different supports [3–5] such as silica, alumina, boria, titania, etc. For oxidation of propane to acrylic acid, MoNbTe(Sb)V mixed oxides appear to be the most promising [6–8]. Molybdenum and vanadium containing heteropoly compounds ($H_{3+x}PMo_{12-x}V_xO_{40}$) were also studied but the selectivity to propene was observed to be low and carbon oxides were the main products. In the latter case the stability of the compounds was the major problem and very often the compounds transformed to lacunary entities or even to a mixture of the constituting oxides. However it is known that alkaline salts of heteropoly compounds are thermally more stable. Moreover the acidity of such compounds is known to be particularly strong which could be detrimental to selective oxidation, although acidity is necessary to activate the poorly reactive alkane. Since molybdenum based heteropolyacids are better catalysts for oxidation reactions than their

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tungsten counterparts [9], we focussed in this work exclusively on molybdenum containing compounds. The activity of these catalysts can also be improved by substituting vanadium for one or two molybdenum cations in the Keggin structure [10–14]. This results in changing the stoichiometric formula from $H_3PMo_{12}O_{40}$ to $H_4PV_1Mo_{11}O_{40}$ or $H_5PV_2Mo_{10}O_{40}$. The higher number of protons balancing the Keggin anion charge is due to the difference in charge for V^V against Mo^{VI}. This substitution can be realised by other cations of different valence such as Co, Ni, Fe, Cu, etc. Various cations can also replace the charge balancing protons to give partially substituted salts of the heteropolyacids such as for the Cs salts, shown to exhibit higher thermal stability [13]. It may also be envisaged to exchange these protons by redox cations such as Co, Ga, Fe, Ni, Sb, Zn, etc. in order to decrease the acidity and increase redox properties of the samples and then to tune redox vs acidic properties. This was the aim of the present study.

2. Experimental

2.1. Sample preparation

$H_4PV_1Mo_{11}O_{40}$ and $Cs_{2.5}H_{1.5}PV_1Mo_{11}O_{40}$ were prepared, according to the following procedures. For $H_4PV_1Mo_{11}O_{40}$ sample, calculated amounts of V_2O_5, MoO_3 and H_3PO_4 were added in a water solution. The solution was stirred, heated up to 80 °C and maintained at this temperature under reflux for 24 h. $H_4PV_1Mo_{11}O_{40}$ sample was obtained by evaporating the solution to dryness at 50 °C.

The $Cs_{2.5}H_{1.5}PV_1Mo_{11}O_{40}$ salt was precipitated by adding the desired amount of Cs_2CO_3 to the aqueous solution of the $H_4PV_1Mo_{11}O_{40}$. The $Cs_{2.5}H_{1.5}PV_1Mo_{11}O_{40}$ sample was obtained by evaporating the solution to dryness at 50 °C.

For the redox metal M samples, the same procedure was followed as for preparing $H_4PV_1Mo_{11}O_{40}$, by preparing a solution of the desired amounts of V_2O_5, MoO_3, H_3PO_4 and $Co(C_5H_7O_2)_2$, $Fe(NO_3)_3$, $Ga(NO_3)_3$, $Ni(NO_3)_2$, Sb_2O_3 or $Zn(NO_3)_2$, in a stoichiometry P:V:M:Mo = 1:1:1:10. The $Cs_{2.5}$ salt was precipitated by adding Cs_2CO_3 as above and the solution evaporated at 50 °C. These cations M were chosen because of their redox and dehydrogenation catalytic properties.

2.2. Infrared spectrometry

The IR spectra were recorded with a Nicolet NEXUS FT-IR spectrometer (spectral range down to 400 cm^{-1}, resolution 2 cm^{-1}). For the study of lattice vibrational bands the samples were diluted (ca. 2 wt.%) and finely ground with KBr and the diffuse reflectance mode was used.

2.3. Catalytic testing

Catalytic study of propane oxidation was performed using a flow micro-reactor (stainless tube 2 cm o.d.) equipped with GC (FID and TCD Detectors) on-line analysis at a temperature in the range 300–400 °C under atmospheric pressure. To control at best the temperature, the thermocouple was installed within the reactor. The gas feed consisted of 40 vol.% propane, 20 vol.% oxygen and He as balance. Total flow rates were 15 or 30 cm^3 min^{-1} and the mass of the catalyst was varied in the range 0.5–0.75 g. Conversion and selectivities were measured after 2 h of reaction at each reaction temperature. No water was introduced in these experiments.

2.4. Thermogravimetric and surface area measurements

TGA measurements were performed using a Setaram TG-DSC 111. BET surface area measurements were performed at liquid nitrogen temperature using a Micromeretics ASAP 2000 equipment after outgassing the sample at 250 °C.

3. Experimental results

The chemical composition of the samples, prepared as described in Section 2.1, determined using a Spectro CIROS SOP 120 ICP atomic emission spectrometer, and surface area values, as measured by BET method, are given in Table 1. It is difficult to know if the additional metal cations M are incorporated in the Keggin structure or are replacing the charge balancing protons or more probably are

Table 1
Chemical analysis by ICP and BET surface area data for the main catalysts

Theoretical composition	Atomic ratio				Surface area (m^2/g)
	Mo	P	V	M	
$H_4PV_1Mo_{11}O_{40}$	11	1	1	0	4
$Cs_{2.5}H_{1.5}PV_1Mo_{11}O_{40}$	11.2	1	1	0	63
$Cs_{2.5}H_{6x-1.5}Ga_{1-x}PV_1Ga_xMo_{11-x}O_{40}$	9.8	1.4	1	0.6	73
$Cs_{2.5}H_{6x-1.5}Sb_{1-x}PV_1Sb_xMo_{11-x}O_{40}$	9.8	1.1	1	0.6	96
$Cs_{2.5}H_{6x-1.5}Fe_{1-x}PV_1Fe_xMo_{11-x}O_{40}$	10.2	1.1	1	–	–
$Cs_{2.5}H_{6x-0.5}Zn_{1-x}PV_1Zn_xMo_{11-x}O_{40}$	9.5	1	1	0.9	92
$Cs_{2.5}H_{6x-0.5}Co_{1-x}PV_1Co_xMo_{11-x}O_{40}$	9.7	1.4	1	0.7	84

partly in both locations. That is why the samples will be designated as $Cs_{2.5}H_{6x-y}M_{1-x}PV_1M_xMo_{11-x}O_{40}$ samples, with M referring to Co, Fe, Ga, Ni, Sb or Zn metal cation, x being the degree of this metal substitution in the Keggin anion and $y = 0.5$, 1.5, 2.5 and 3.5 for di-, tri-, quadri- and pentavalent metal M cations, respectively.

To try to answer the question of substitution and/or cationic exchange, two techniques can be used, namely thermogravimetry and FT-IR. In the first technique the amount of water desorbed in the 200–450 °C range, could be assigned to dehydroxylation (so-called loss of constitutional water) of the HPA giving its anhydrous form, while some downward shift of the IR Mo–O bands and splitting of the P–O band can be expected if the metal element is incorporated in the Keggin anion [15,16].

3.1. FT-IR study

The IR spectra of heteropolyoxometallates have been discussed and bands assigned previously [15,16]. The most relevant features are as follows: ν_{as}(P–O$_a$) (1080–1060 cm^{-1}), ν_{as}(Mo–O$_d$) (990–960 cm^{-1}), ν_{as}(Mo–O$_b$–Mo) (900–870 cm^{-1}) and ν_{as}(Mo–O$_c$–Mo) (810–760 cm^{-1}), where O$_a$ refers to O atom common to PO$_4$ tetrahedron and a trimetallic group; O$_b$ to the O atom connecting two trimetallic groups; O$_c$ to the O atom connecting two MoO$_6$ octahedra inside a trimetallic group and O$_d$ to the terminal O atom is shown in Fig. 1. The ν_{as}(Mo–O$_b$–Mo) mode is particularly sensitive to hydration degree due to hydrogen bonding which decreases the Mo–O bond strength and thus the vibration frequency and to the nature of cations exchanging protons for the same reason. Vibrational mode spectra of 1-metallo-11-molydophosphates $PM^{n+}Mo_{11}O_{40}{}^{(9-n)-}$ related to Keggin structure have been reported and discussed as a function of the nature of a metal M^{n+} ($n < 6$), considered as a perturbing element [15,16]. This element was observed to induce a decrease in ν_{as}(Mo–O$_d$) stretching frequency, thus a weakening of the Mo–O$_d$ bond and a possible splitting of ν_{as}(P–O$_a$) band. The protons were suggested to be localised on the most highly charged O atoms, namely the O$_b$ atoms. A change in the ν_{as}(Mo–O$_b$–Mo) frequency is thus expected upon dehydration or exchanging protons by other cations, as it was clearly shown in an in situ study of $Cs_{2.5}H_{1.5}W_{12}O_{40}$ samples [17].

Typical IR spectra of non-dehydrated samples are shown in Fig. 2, while the positions of the main bands are given in Tables 2 and 3, for comparison of the effect of V substitution for Mo in the acid form and Cs exchange for protons (Table 2) in order to try to interpret data for M^{n+} cation (substitution vs cationic

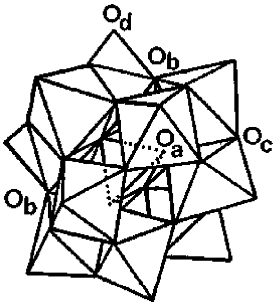


Fig. 1. Schematic representation of a Keggin anion for IR band assignment taken from Ref. [16].

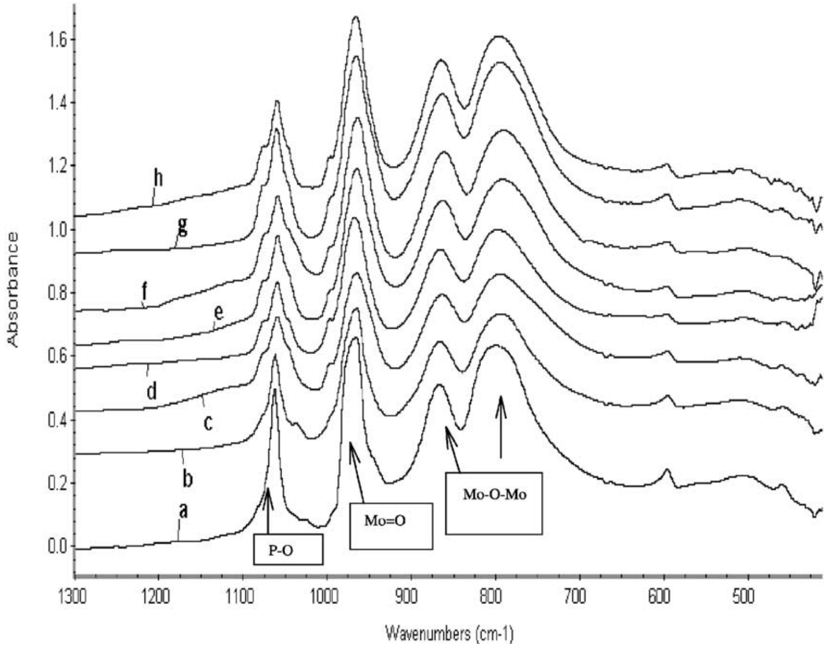


Fig. 2. FT-IR spectra of samples before catalytic reaction: (a) $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$; (b) $Cs_{2.5}H_{1.5}PV_1Mo_{11}O_{40}$; (c) $Cs_{2.5}H_{6x-1.5}Ga_{1-x}PV_1Ga_xMo_{11-x}O_{40}$; (d) $Cs_{2.5}H_{6x-1.5}Sb_{1-x}PV_1Sb_xMo_{11-x}O_{40}$; (e) $Cs_{2.5}H_{6x-0.5}Ni_{1-x}PV_1Ni_xMo_{11-x}O_{40}$; (f) $Cs_{2.5}H_{6x-1.5}Fe_{1-x}PV_1Fe_xMo_{11-x}O_{40}$; (g) $Cs_{2.5}H_{6x-0.5}Zn_{1-x}PV_1Zn_xMo_{11-x}O_{40}$; (h) $Cs_{2.5}H_{6x-0.5}Co_{1-x}PV_1Co_xMo_{11-x}O_{40}$.

exchange). It appears that when V is incorporated in the acid form (0–3 per Keggin unit), ν_{as}(P–O$_a$) decreases from 1064 to 1059 cm^{-1}, ν_{as}(Mo–O$_b$–Mo) from 968 to 962 cm^{-1}, ν_{as}(Mo–O$_c$–Mo) from 789 to 783 cm^{-1}, while ν_{as}(Mo–O$_d$) remains about constant. When Cs exchange protons, ν_{as}(P–O$_a$) decreases from 1062 to 1059 cm^{-1}, ν_{as}(Mo–O$_d$) increases from 964 to 966 cm^{-1}, ν_{as}(Mo–O$_b$–Mo) remains about constant, while ν_{as}(Mo–O$_c$–Mo) increases. In the latter case the effect of exchange and substitution is opposite. For instance for V = 0, ν_{as}(Mo–O$_c$–Mo) varies from 789 to 800 cm^{-1}, for V = 1 from 785 to 794 cm^{-1} and for V = 2 from 781 to 799 cm^{-1} (Table 2).

When a metal cation M is added these opposite trends makes any conclusion difficult for the differentiation between exchange and substitution. However these general trends allowed us to conclude from the data given in Table 3 that for the redox metal cation samples both substitution and exchange of protons by the metal cation did occur.

Table 2
IR data in cm^{-1} for acid and $Cs_{2.5}$ salts vs V incorporation in the Keggin anion

Samples	ν_{as}(P–O$_a$) ± 2 cm^{-1}	ν_{as}(Mo–O$_d$) ± 2 cm^{-1}	ν_{as}(Mo–O$_b$–Mo) ± 5 cm^{-1}	ν_{as}(Mo–O$_c$–Mo) ± 5 cm^{-1}
$H_3PMo_{12}O_{40}$	1064	962	868	789
$H_4PV_1Mo_{11}O_{40}$	1063	962 (996[a])	867	785
$H_5PV_2Mo_{10}O_{40}$	1060	961 (996[a])	862	781
$H_6PV_3Mo_9O_{40}$	1059	961 (995[a])	864	783
$Cs_{2.5}H_{0.5}PMo_{12}O_{40}$	1062 (1026[a])	966	866	800
$Cs_{2.5}H_{1.5}V_1Mo_{11}O_{40}$	1062 (1037[a])	964 (997[a])	866	794
$Cs_{2.5}H_{2.5}PV_2Mo_{10}O_{40}$	1059 (1074[a])	970 (997[a])	868	799

[a] Indicates a shoulder on the main band.

Table 3
IR data in cm^{-1} for the main heteropolyacid salt samples before catalytic reaction

Samples	ν_{as}(P–O$_a$) ± 2 cm^{-1}	ν_{as}(Mo–O$_d$) ± 2 cm^{-1}	ν_{as}(Mo–O$_b$–Mo) ± 5 cm^{-1}	ν_{as}(Mo–O$_c$–Mo) ± 5 cm^{-1}
$H_3PMo_{12}O_{40}$	1064	962	868	789
$H_4PV_1Mo_{11}O_{40}$	1063	962 (996^a)	867	785
$Cs_{2.5}H_{1.5}PV_1Mo_{11}O_{40}$	1062 (1037^a)	964 (997^a)	866	794
$Cs_{2.5}H_{6x-1.5}Ga_{1-x}PV_1Ga_xMo_{11-x}O_{40}$	1060 (1076^a)	965 (996^a)	864	795
$Cs_{2.5}H_{6x-1.5}Sb_{1-x}PV_1Sb_xMo_{11-x}O_{40}$	1060 (1077^a)	968 (997^a)	866	798
$Cs_{2.5}H_{6x-0.5}Ni_{1-x}PV_1Ni_xMo_{11-x}O_{40}$	1059 (1077)	965 (996^a)	863	790
$Cs_{2.5}H_{6x-1.5}Fe_{1-x}PV_1Fe_xMo_{11-x}O_{40}$	1059 (1075^a)	964 (996^a)	862	790
$Cs_{2.5}H_{6x-0.5}Zn_{1-x}PV_1Zn_xMo_{11-x}O_{40}$	1061 (1076^a)	966 (996^a)	864	795
$Cs_{2.5}H_{6x-0.5}Co_{1-x}PV_1Co_xMo_{11-x}O_{40}$	1060 (1077^a)	966 (996^a)	865	796

[a] Designates a shoulder in the main band.

In addition some shoulders or even small bands appear at 1075–1077 cm^{-1} and at 996 cm^{-1} upon addition of the metal M cations, which may indicate at least partial substitution of Mo by these metal M cations [16]. That is why the exact chemical formula could not be established precisely and why we had to write $Cs_{2.5}H_{6x-y}M_{1-x}PV_1M_xMo_{11-x}O_{40}$ as a general chemical formula. The band at 996 cm^{-1} was also assigned to some MoO_3 which was not incorporated in the Keggin anion.

After 12 h continuous catalytic testing in the 300–400 °C temperature range, the samples were again analysed by IR spectroscopy. Some spectra are shown in Fig. 3, while the position of the bands is reported in Table 4. It appears that $H_4PV_1Mo_{11}O_{40}$ compound has lost partly its Keggin structure, while all Cs samples have not, which shows that only the Cs salts are stable enough in our catalytic conditions. Moreover, the ν_{as}(P–O$_a$) frequencies shifted toward higher wavenumber values, which indicates that some substituted atoms (V and/or M) have been extracted from the Keggin cell and have presumably taken an exchange cation location. This was already observed for a $PV_1Mo_{11}O_{40}$ sample used for isobutyric acid ODH to methacrylic acid on Cu/$H_4PV_1Mo_{11}$ material at 400 °C [12,14].

3.2. Thermogravimetric data

Typical curves are shown in Fig. 4 for $Cs_{2.5}H_{1.5}PV_1Mo_{11}O_{40}$ and $Cs_{2.5}H_{6x-1.5}Fe_{1-x}PV_1Fe_xMo_{11-x}O_{40}$ samples. Their shape is typical of the loss of constitutional water in the 150–500 °C temperature range, although the plateaux are not as well defined as for the acidic form $H_3PMo_{12}O_{40}$ and $H_4PV_1Mo_{11}O_{40}$ samples. From the amount of water released in the 200–450 °C temperature range, one can calculate the number of protons. The data given in Table 5

Table 4
IR data in cm^{-1} of the main heteropolyacid salt samples after 12 h catalytic reaction

Samples	ν_{as}(P–O$_a$) ± 2 cm^{-1}	ν_{as}(Mo–O$_d$) ± 2 cm^{-1}	ν_{as}(Mo–O$_b$–Mo) ± 5 cm^{-1}	ν_{as}(Mo–O$_c$–Mo) ± 5 cm^{-1}
$H_4PV_1Mo_{11}O_{40}$	1064	963 (997^a)	868	785
$Cs_{2.5}H_{1.5}PV_1Mo_{11}O_{40}$	1063 (1036^a)	967 (997^a)	867	800
$Cs_{2.5}H_{6x-1.5}Ga_{1-x}PV_1Ga_xMo_{11-x}O_{40}$	1060 (1075^a)	964 (997^a)	864	793
$Cs_{2.5}H_{6x-1.5}Sb_{1-x}PV_1Sb_xMo_{11-x}O_{40}$	1063 (1033^a)	969	868	801
$Cs_{2.5}H_{6x-0.5}Ni_{1-x}PV_1Ni_xMo_{11-x}O_{40}$	1060 (1075^a)	964 (997^a)	862	777
$Cs_{2.5}H_{6x-1.5}Fe_{1-x}PV_1Fe_xMo_{11-x}O_{40}$	1062 (1075^a, 1037^a)	965	864	790
$Cs_{2.5}H_{6x-0.5}Zn_{1-x}PV_1Zn_xMo_{11-x}O_{40}$	1062 (1076^a, 1033^a)	965 (996^a, 1013^a)	868	790
$Cs_{2.5}H_{6x-0.5}Co_{1-x}PV_1Co_xMo_{11-x}O_{40}$	1061 (1075^a)	965 (996)	864	788

[a] Designates a shoulder in the main band.

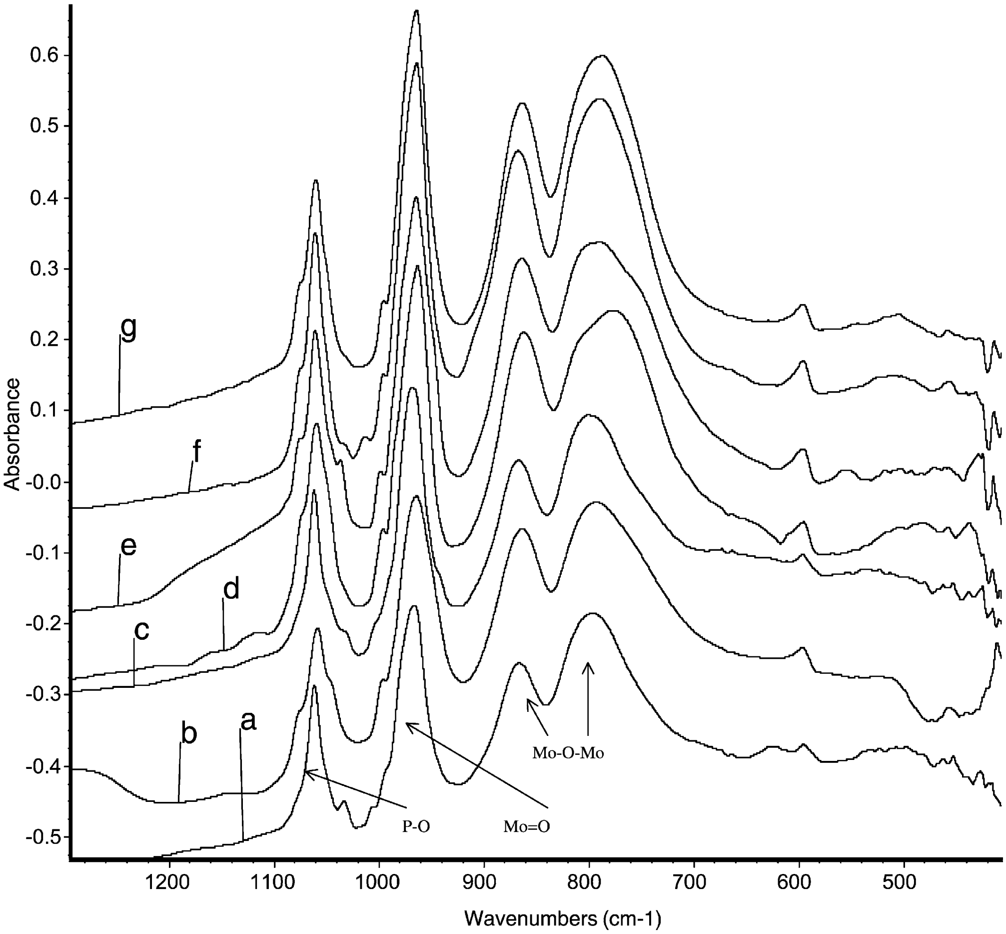


Fig. 3. FT-IR spectra of samples after 12 h of catalytic reaction: (a) $Cs_{2.5}H_{1.5}PV_1Mo_{11}O_{40}$; (b) $Cs_{2.5}H_{6x-1.5}Ga_{1-x}PV_1Ga_xMo_{11-x}O_{40}$; (c) $Cs_{2.5}H_{6x-1.5}Sb_{1-x}PV_1Sb_xMo_{11-x}O_{40}$; (d) $Cs_{2.5}H_{6x-0.5}Ni_{1-x}PV_1Ni_xMo_{11-x}O_{40}$; (e) $Cs_{2.5}H_{6x-1.5}Fe_{1-x}PV_1Fe_xMo_{11-x}O_{40}$; (f) $Cs_{2.5}H_{6x-0.5}Zn_{1-x}PV_1Zn_xMo_{11-x}O_{40}$; (g) $Cs_{2.5}H_{6x-0.5}Co_{1-x}PV_1Co_xMo_{11-x}O_{40}$.

are quite coherent with the theoretical value of protons, in particular for the $H_4PV_1Mo_{11}O_{40}$ and $Cs_{2.5}H_{1.5}PV_1Mo_{11}O_{40}$ samples, which made us confident in the method. If these values and this approach are correct, one can even evaluate the degree x of metal M cation substitution in the Keggin anion. The values of x are given in Table 5, last column. Even if this approach is questionable and to be taken with caution and the values rather imprecise, it indicates clearly that actually some metal cation M substitution did occur. Unfortunately, we are not equipped with an outgassing in situ system to study self-supported wafers in the hydroxyl region (3400–3800 cm^{-1}), which would have strengthened our TGA experiment conclusions.

Table 5
Calculation of H^+ content per Keggin unit (KU) from water released between 200 and 450 °C determined by TGA analysis[a]

Samples	H^+/KU	x
$Cs_{2.5}H_{6x-1.5}Ga_{1-x}PV_1Ga_xMo_{11-x}O_{40}$	2.1	0.6
$Cs_{2.5}H_{6x-1.5}Sb_{1-x}PV_1Sb_xMo_{11-x}O_{40}$	3	0.75
$Cs_{2.5}H_{6x-0.5}Ni_{1-x}PV_1Ni_xMo_{11-x}O_{40}$	2.4	0.48
$Cs_{2.5}H_{6x-1.5}Fe_{1-x}PV_1Fe_xMo_{11-x}O_{40}$	1.9	0.57
$Cs_{2.5}H_{6x-0.5}Zn_{1-x}PV_1Zn_xMo_{11-x}O_{40}$	1.4	0.32
$Cs_{2.5}H_{6x-0.5}Co_{1-x}PV_1Co_xMo_{11-x}O_{40}$	2.3	0.47
$Cs_{2.5}H_{1.5}PV_1Mo_{11}O_{40}$	1.6	0
$H_4PV_1Mo_{11}O_{40}$	3.9	0

[a] The values of x are then calculated from the chemical formula assuming that the metal cations have kept their starting oxidation state, i.e. are not hydrolysed.

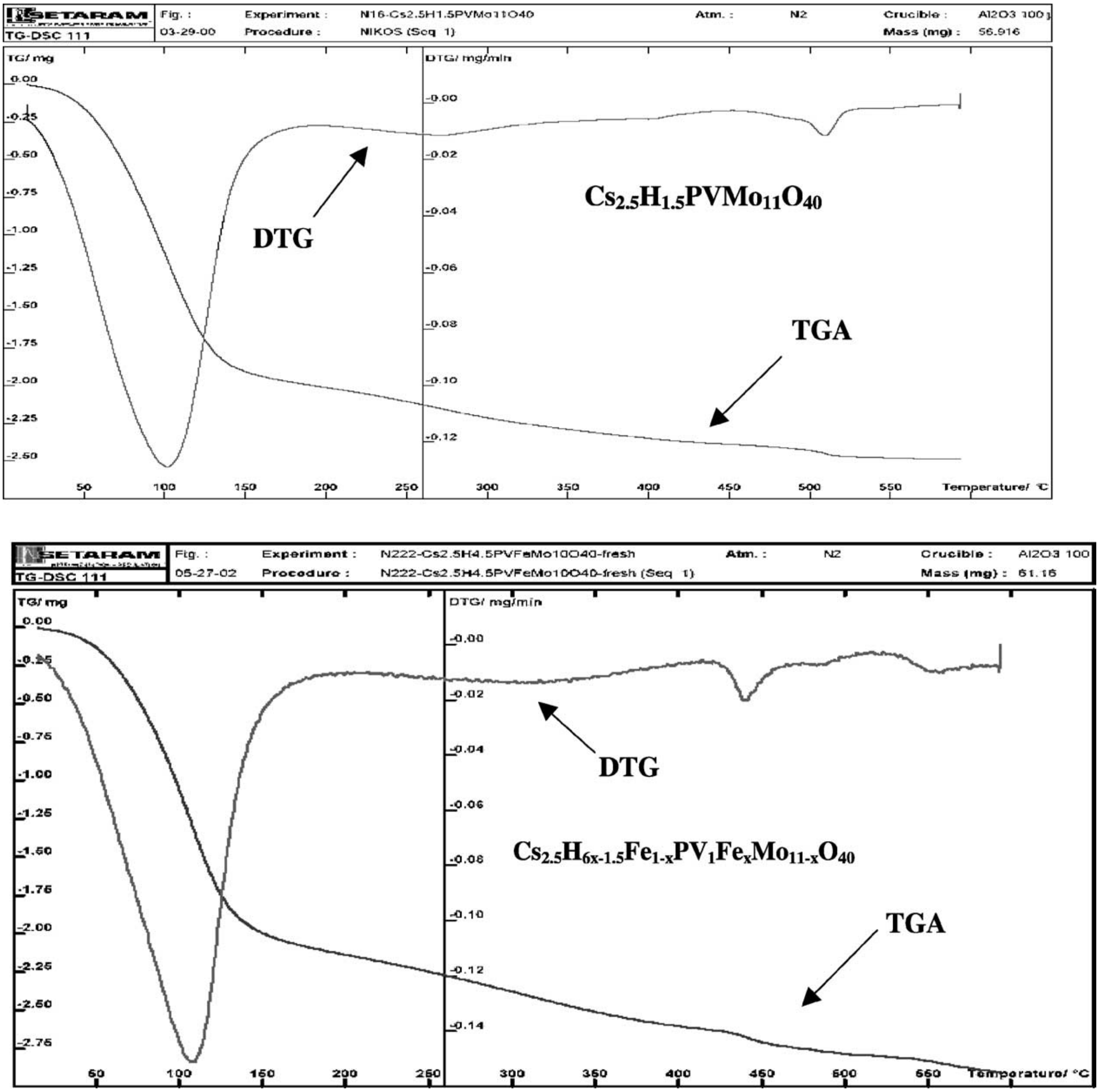


Fig. 4. TGA and DTG curves of $Cs_{2.5}H_{1.5}PV_1Mo_{11}O_{40}$ and $Cs_{2.5}H_{6x-1.5}Fe_{1-x}PV_1Fe_xMo_{11-x}O_{40}$ samples.

3.3. Catalytic testing

Testing was performed in the range 300–400 °C at the conditions described in the experimental section. Propene, acetic acid, acrylic acid and CO_x were the major products detected, although acetic and acrylic acids were rather minor products. No methane and ethane were detected. It is worth noticing that the catalysts were observed to react at relatively low temperature (300–400 °C) compared to VMgO or supported V_2O_5 catalysts, which work at 500–550 °C.

Fig. 5 shows the variations of selectivities vs conversion for $Cs_{2.5}H_{6x-0.5}Zn_{1-x}PV_1Zn_xMo_{11-x}O_{40}$ sample taken as an example. In this experiment the

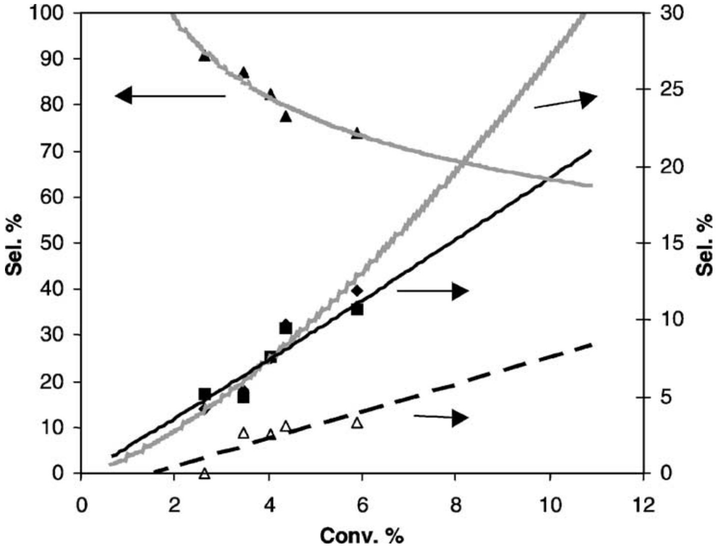
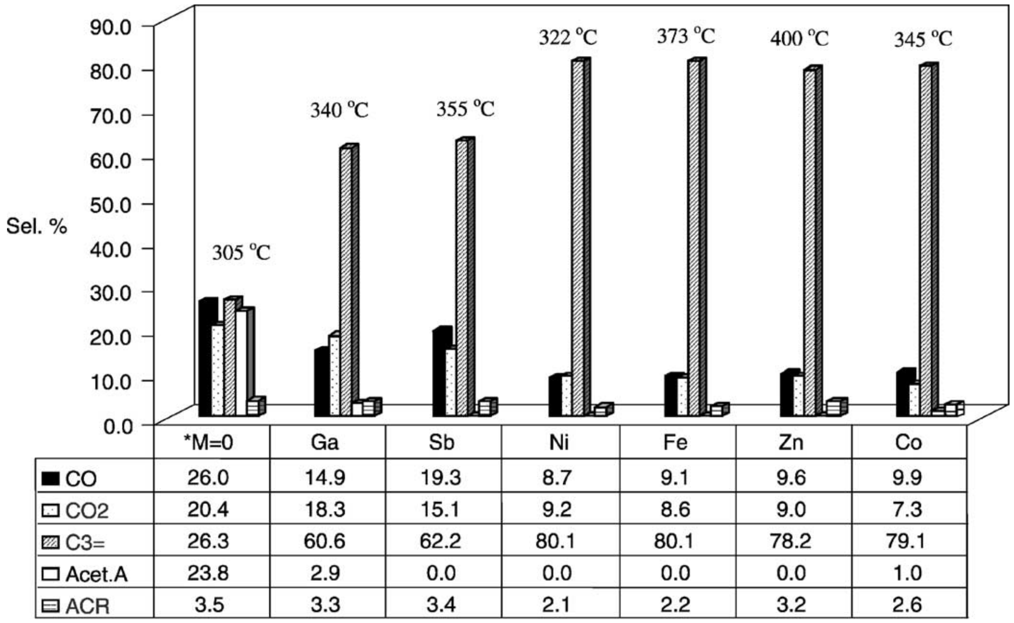


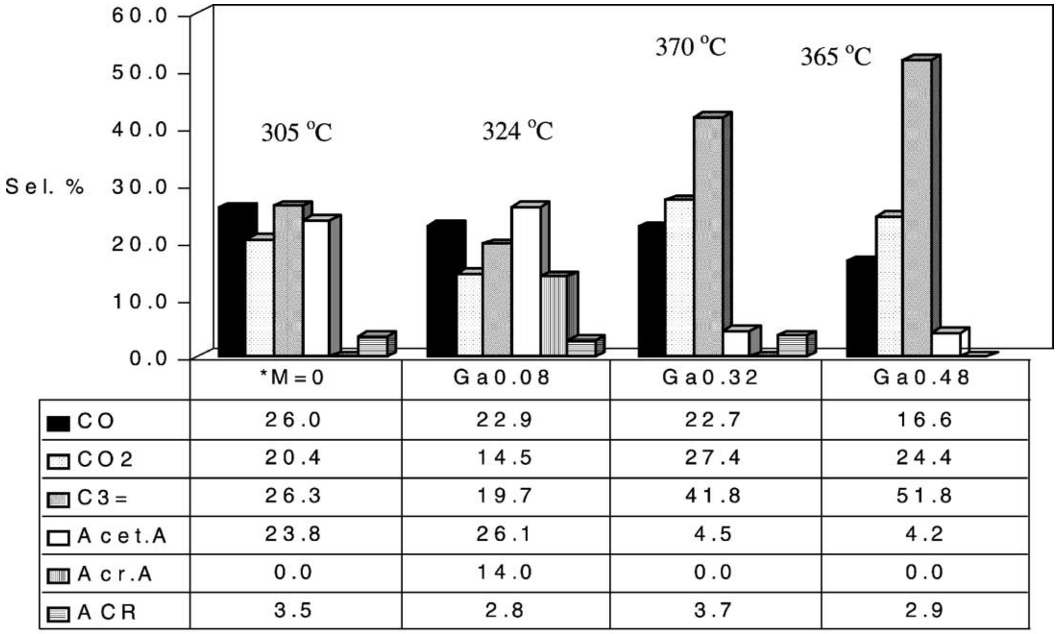
Fig. 5. Variations of the selectivities in different products as a function of propane conversion, controlled by increasing the reaction temperature from 340 to 400 °C. Sample $Cs_{2.5}H_{6x-0.5}Zn_{1-x}PV_1Zn_xMo_{11-x}O_{40}$. Reaction conditions: C_3:O_2:He = 2:1:2, flow rate: 15 $cm^3\,min^{-1}$. Selectivities to CO (◆), CO_2 (■), $C_3{}^{=}$ (▲), ACR (△).



	*M=0	Ga	Sb	Ni	Fe	Zn	Co
■ CO	26.0	14.9	19.3	8.7	9.1	9.6	9.9
▒ CO2	20.4	18.3	15.1	9.2	8.6	9.0	7.3
▨ C3=	26.3	60.6	62.2	80.1	80.1	78.2	79.1
□ Acet.A	23.8	2.9	0.0	0.0	0.0	0.0	1.0
▤ ACR	3.5	3.3	3.4	2.1	2.2	3.2	2.6

* $Cs_{2.5}H_{1.5}PVMo_{11}$

Fig. 6. Variations in selectivities of $Cs_{2.5}H_{6x-y}M_{1-x}PV_1M_xMo_{11-x}O_{40}$ samples at 5% propane conversion as a function of the metal cation M. The reaction temperature to reach 5% conversion is indicated on top of each bar diagram.



	*M = 0	Ga0.08	Ga0.32	Ga0.48
■ CO	26.0	22.9	22.7	16.6
▨ CO2	20.4	14.5	27.4	24.4
▩ C3=	26.3	19.7	41.8	51.8
□ Acet.A	23.8	26.1	4.5	4.2
▥ Acr.A	0.0	14.0	0.0	0.0
▤ ACR	3.5	2.8	3.7	2.9

*$Cs_{2.5}H_{1.5}PVMo_{11}$

Fig. 7. Variations in selectivities of $Cs_{2.5}H_{1.5}PV_1Mo_{11}O_{40}$ sample at 5% propane conversion as a function of protons being replaced (exchanged) by increasing amount of Ga cation. The reaction temperature to reach 5% conversion is indicated on top of each bar diagram.

reaction temperature was varied in order to change the conversion, but it was checked that this affects only slightly the results by changing the space velocity, i.e. the contact time, at the same temperature (360 °C). As expected selectivity to propene decreased with the conversion, while that in CO_x increased at the expense of propene. No formation of acetic acid was observed, while small amounts of acrolein were detected. A similar catalytic behaviour was observed for the other samples.

In order to get data reliable for comparing the behaviour of the different samples experimental data are shown in Figs. 6 and 7 at 5% conversion. It is clear from Fig. 6 that introducing a metal cation M led to much more propene formation (60–80% selectivity) and low acetic acid and CO_x formation. The same effect was observed at 10% conversion. The beneficial effect of redox metal cation M on the oxidation properties of heteropolyoxometallate compounds was already observed in many cases [18,19]. For instance, iron was found the most attractive redox element for propane [20] and isobutane [21,22] selective oxidation to acrylic or isobutyric acids, respectively. Moreover when the protons of $Cs_{2.5}H_{1.5}PV_1Mo_{11}O_{40}$ sample were progressively exchanged by Ga cation (Fig. 7) selectivity in propene was observed to increase and that in CO_x and acetic acid to decrease. However, in the latter case, selectivity in propene did not reach that observed when Ga was incorporated during the synthesis, as if the samples were still strongly acidic. It is quite possible that protons are not exchanged by Ga^{3+} cation but by $Ga(OH)^{2+}$ or even $Ga(OH)_2{}^+$ cations which then neutralise less protons. Bénézeth et al. [23] have shown that the distribution of Ga cationic species in solution depends strongly on the pH and temperature. At pH = 3 and 30 °C, usually used for cationic exchange, the Ga speciation is strongly dominated by highly charged species (50% Ga^{3+} and 50% $Ga(OH)^{2+}$), while at 150 °C one has 60% $Ga(OH)_2{}^+$. In our case the pH of the solution was less than 2 to avoid the formation of lacunary Keggin anions [13] but the solution was heated to 50 °C for evaporating the water solvent. Such a possibility of the proton exchange by Ga hydroxy cation rather than Ga^{3+} was supported by TGA measurements of Ga exchanged samples, which exhibited a much higher amount of protons than normally expected if three protons were exchanged by one Ga^{3+} cation.

It is clear that our data show that acid and redox properties of heteropolyoxometallates materials influence greatly their catalytic properties for ODH and selective oxidation of propane. These acid and redox properties can be tuned but it appears that for this purpose direct synthesis is more appropriate than post-synthesis cationic exchange.

Another interesting observation is that, among the oxygenates, acetic acid was formed rather than acrylic acid. The mechanism of propane selective oxidation has been widely discussed in the literature [8,24,25]. Recently, one of us [26] has shown that in propane oxidation to acrylic and acetic acids on MoNbSbV mixed oxides, the formation of acetic acid at the expense of acrylic acid was related to the presence of strong Brønsted sites. It is not surprising that acetic acid was formed presently, particularly in the absence of an additional redox metal M cation and its formation decreased when protons were exchanged with these redox metal M cations. This obviously holds true also for CO_x formation. The influence of strong Brønsted acidity observed in propane oxidation to acetic acid was also mentioned on heteropolyacid salts [27] and on vanadyl exchanged beta zeolite [28].

4. Conclusion

The present study has shown that redox elements such as Co, Fe, Ga, Ni, Sb or Zn are partly substituted during synthesis to Mo^{VI} in a $Cs_{2.5}H_{1.5}PV_1Mo_{11}O_{40}$ material, the remaining part being in a cationic exchange position. This leads to catalysts quite active in propane ODH to propene at relatively low temperature (300–400 °C). It has also been shown that using Cs salts leads to catalysts stable under our catalytic conditions. Relative acidity (via Keggin anion metallic substitution) and redox properties by exchanged cations replacing the protons either during synthesis or post-synthesis can be tuned. However, it was also shown that the direct synthesis process was more efficient than post-synthesis cationic exchange. The main conclusion is that one can get a quite high selectivity in propene at relatively low temperature and keep the heteropolyacid salt stable under catalytic conditions by using the $Cs_{2.5}$ salt of the V_1 substituted material and exchanging protons by a redox metal.

Moreover, it is shown that Brønsted acidity remains quite strong leading to acetic acid rather than acrylic acid during propane selective oxidation. At variance this acidity permits propane to be activated at relatively low temperature, i.e. to get high selectivity in propene if redox cations replace majority of protons. The main conclusion is that the number of strong Brønsted acid sites and redox properties can be easily tuned for such systems, which results in promising properties for eventual substitution of propane dehydrogenation in the current industrial processes by ODH.

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