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Effect of Au in $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ and $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}/Au/TiO_2$ catalysts in the gas phase oxidation of propylene

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Abstract

The catalytic study of the gas phase oxidation of propylene has been carried out using heteropolyacids modified with gold. In addition, TiO_2 was used as the main support for heteropolyacids and gold. Propylene oxidation was performed under different reaction conditions and in all the cases water was introduced owing to the beneficial effect in the formation of oxygenated products. It was found that deposition methods of Au onto heteropolyacid and heat pre-treatment procedure significantly affected the activity and the distribution of the products: sol immobilization promoted the total oxidation, whereas impregnation method the selective oxidation mainly to acrolein and acetic acid, depending on other reaction conditions. Depositing $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ salt onto a preformed 1.5%Au/TiO_2 a significant increase towards the formation of oxygenated products was observed at the expense of total combustion. In particular, acrolein was produced in a synergistic manner. FT-IR, XRD, XPS and TPR techniques were used for catalyst characterization.

Keywords: Gas phase oxidation of propylene; Heteropolyacids; Gold; Titania; Promoters

1. Introduction

The transformation of alkanes/alkenes to useful intermediates is of significant importance in the chemical industry. This transformation is carried out in gas phase on solid catalyst with the simultaneous presence of the alkane/alkene and the molecular oxygen. Examples based on this concept are the commercial processes for the production of maleic anhydride from *n*-butane using vanadyl pyrophosphate (VPO) catalysts [1–4] and for the production of acrylic acid using multi-component oxides [5–8]. In the first example, the most important advantages for substituting alkanes/alkenes to aromatics are the one-stage process, the lower cost and the reduced environment impact. However, a drawback of this process is the low yield to the desired oxygenated products, making this process less profitable.

In academia, a great deal of research has been focused on the selective oxidation of alkane/alkene to acrylic acid. A variety of catalytic systems have been already explored. The main catalytic systems are based on metal exchanged heteropolyacids [9–22], vanadyl pyrophosphates [10,23–28] and multi-component oxides [29,10,30–38]. It has been shown that the acid-redox properties of each catalytic system affect considerably the activity and distributions of the products.

It is well known that Au nanoparticles deposited on Ce_3O_4, NiO, MnO_x, Fe_2O_3 and TiO_2 are active components in total combustion of C_1–C_4 hydrocarbons rather than in selective oxidation [39–41]. Nevertheless, some reports dealing with the partial oxidation of hydrocarbons in the presence of Au catalysts [42–44] indicate the usefulness of gold catalysis in selective oxidation for chemical synthesis.

In the present study, we have investigated the catalytic properties of gold promoted heteropolyacid derivatives in propene conversion. For this purpose, we synthesized heteropolyacid salts having a Keggin type structure and the influence of gold addition was studied. Preliminary results using a more

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complex catalytic system (Au/TiO_2 + heteropolyacids) are also presented.

2. Experimental

2.1. Catalyst preparation

2.1.1. Heteropolyacids

$H_4PVMo_{11}O_{40}$ and $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ samples were prepared according to the following procedure.

2.1.1.1. $H_4PVMo_{11}O_{40}$ synthesis. In a round bottom flask of 500 ml, the desired amounts of MoO_3, V_2O_5 and H_3PO_4 were added in a 250 ml aqueous solution. The mixture was refluxed for 24 h and a clear dark-orange colour solution was formed. Prior to the evaporation at 50 °C, the solution was filtered for the removal of residues. The $H_4PVMo_{11}O_{40}$ sample was collected by evaporation of the solvent and dried at 120 °C for 12 h.

2.1.1.2. $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ synthesis

To an aqueous solution of $H_4PVMo_{11}O_{40}$ was added the desired amount of Cs_2CO_3 dropwise. Precipitation was occurred and the solution was evaporated at 50 °C. The powder was collected and dried at 120 °C for 12 h. For the heat pre-treatment of the samples two different procedures were used.

2.1.1.2.1. Procedure A. The powder was treated in situ in the reactor at 300 °C under N_2/O_2 flow for 5 h prior to the reaction.

2.1.1.2.2. Procedure B. The powder was treated in situ in the reactor at 300 °C under H_2 flow for 2 h prior to the reaction.

2.1.2. Modified $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ with Au

For the modified $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ samples, the dried $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ sample was used in the following procedures.

2.1.2.1. Procedure A′: impregnation method. Addition of $HAuCl_4$ solution on a $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ slurry was performed. Prior to the addition of $HAuCl_4$, HCl was added in order to keep the pH close to 2. The slurry was evaporated until dryness at 50 °C. The powder was collected and dried at 120 °C in an oven for 12 h. The powder was treated in situ in the reactor at 300 °C under N_2/O_2 flow for 5 h prior to the reaction.

2.1.2.2. Procedure B′: impregnation method. Addition of $HAuCl_4$ solution on a $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ slurry was performed. Prior to the addition, HCl was added in order to keep the pH close to 2. The slurry was evaporated until dryness at 50 °C. The powder was collected and dried at 120 °C in an oven for 12 h. The powder was treated in situ in the reactor at 300 °C under H_2 flow for 2 h prior to the reaction.

2.1.2.3. Procedure C: addition of Au sol ($PVA/NaBH_4$). In this method, an Au sol was prepared by reducing the $HAuCl_4$ precursor with $NaBH_4$. Prior to the reduction PVA was added as a protective agent. $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ was dispersed to an aqueous solution. Prior to the addition of the Au sol, HCl was added in order to keep the pH close to 2. Au sol was added on the $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ slurry. The mixture was kept under stirring overnight and it was evaporated until dryness at 50 °C. The powder was collected and dried at 120 °C in an oven for 12 h.

2.1.3. Physical mixtures of 1.5%Au/TiO_2 with $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$

Physical mixtures of 1.5%Au/TiO_2 (supplied from World Gold Council, Lot No. 02-5) with $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ were made. The titania-gold supported catalysts were prepared by the deposition precipitation method using P-25 (supplied by Degussa) powder as the TiO_2 support. The gold content was 1.5% and the average gold particle size was 3.7 nm (standard variation 1.5 nm). The loading of $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ was 20 wt.%. An amount of $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ was ground with 1.5% Au/TiO_2 in a pestle and mortar. The pre-treatment of the resulting catalysts was performed in situ. For 1.5%Au/TiO_2/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$, the heat pre-treatment temperature was at 300 °C for 2 h under N_2/O_2 flow.

2.2. Characterization of the catalysts

The characterization of the samples was performed using FT-IR, XRD, XPS techniques.

The samples were characterized by IR spectroscopy, lattice vibration modes in the 700–1100 cm^{-1} range being typical of Keggin anion [21,22,45,46]. The FT-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. 1 wt.%) and finely ground with dried KBr and the transmission mode was used.

X-ray diffraction patterns (XRD) were collected using a Rigaku D III-MAX horizontal-scan powder equipped with a graphite monochromator, operating at 40 kV and 45 mA, and employing nickel-filtered Cu Kα radiation ($\lambda = 0.1542$ nm).

XPS measurements were performed in a M-Probe Instrument (SSI) equipped with a monochromatic Al Kα source (1486.6 eV) with a spot size of 200μm × 750 μm and a pass energy of 25 eV, providing a resolution for 0.74 eV. The accuracy of the reported binding energies (BE) can be estimated to be ±0.2 eV. The quantitative data were checked accurately and reproduced several times (at least 10 times for each sample).

H_2-TPR measurements were performed using a Micromeritics Pulse Chemisorb 2700 apparatus. Appropriate amount of samples (in order to keep constant the pseudo contact time with respect to heteropolyacid content) was treated at 400 °C for 1 h in pure oxygen flow (50 ml/min) in a pyrex fixed-bed micro-reactor, cooled down to −78 °C (dry ice) in Ar flow. TPR experiment was conducted on calcined sample heating, with rate of 8 °C/min to 500 °C in a H_2 (5% by volome)/Ar mixture.

2.3. Catalytic testing

The catalytic experiments were carried out in a glass pyrex reactor (i.d., 12 mm, length 200 mm) working at atmospheric pressure. The catalysts bed was at the bottom of the reactor. The temperature was controlled and monitored by a thermocouple placed in contact with the bed. The feed consisted of a mixture of propylene, oxygen and nitrogen. H_2O was introduced on the top of the reactor by using a mini-pump. The total flow rate was 20 ml/min resulting in a gas hourly space velocity (GHSV) of 2400 h^{-1} (0.5 ml, i.e. 0.75 g, of sample used). Reaction temperature was in the range of 220–300 °C. Analysis of the gas products was performed on line by using a gas chromatography (HP5890 II). Analysis of the liquid products was performed off line by condensation of the liquid products at the outlet of the reactor using an ice-cooled trap. For the analysis of the products a Porapaq Q column (15 m × 0.32 mm) was used, connected with a TCD detector. Conversion was calculated on the basis of the measurement of the inlet reactant feed and outlet. Selectivity towards a product was calculated as the fraction of the moles of C in the product with respect to the total moles of C in all products. The moles of C were defined as the number of moles multiplied by the number of C atoms in the reactant/product. Reported data are the values obtained after 4 h on stream.

3. Results and discussion

3.1. Characterization

3.1.1. FT-IR spectroscopy

IR spectra of the unmodified (dried sample)and modified $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ samples (A′, B′, C) are shown in Figs. 1 and 2 before and after catalytic reaction, respectively, whereas the position of the main bands are given in Tables 1 and 2. Typical bands observed for the Keggin structure are in the range (700–1200) cm^{-1}. The bands between (1080–1060 cm^{-1}), (990–960 cm^{-1}), (900–870 cm^{-1}) and (810–760 cm^{-1}) are attributed to ν_{as}(P-O_a), ν_{as}(Mo-O_d), ν_{as}(Mo-O_b-Mo) and ν_{as}(Mo-O_c-Mo) vibrational modes, respectively. It can be seen that the addition of Au did not modify the Keggin structure, since no alteration in the position of the peaks was found. Comparison with the samples after catalytic reaction revealed that the Keggin structure remained almost stable, since only slight shifts in the frequencies were observed, due to the partial dehydration of the samples [47].

Figs. 3 and 4 show the IR spectra of the physical mixtures of the 1.5%Au/TiO_2/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ with respect to the 1.5%Au/TiO_2 and the $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ dried samples, before and after catalytic reaction, respectively. Also in this case there was no modification of the spectra before and after the catalytic reaction. The main bands observed for the $Cs_{2.5}$ salt deposited on 1.5%Au/TiO_2 sample, are at 1062 and 967 cm^{-1}, in agreement with the bands observed for the pure $Cs_{2.5}$ salt, whereas the other bands are masked by the broad band of the support [48]. Therefore, the IR spectra indicate that $Cs_{2.5}$ salt structure is maintained in all the tested catalysts.

3.1.2. XRD

For the $Cs_{2.5}$ samples the main observed peaks were at $2\theta = 10.6°$, 18.4°, 23.8°, 26.1°, 30.3°, 35.6° and 38.9°, which are assigned to the cubic phase [49]. There was no modification in the XRD patterns of the used samples, indicating that there was no structural change in the heteropoly compounds. As an example the XRD patterns of the unmodified (dried) and modified (A′, B′, C)1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ samples before and after catalytic reaction are shown in Fig. 5. These results are in agreement with the data from the FT-IR study, showing that under these conditions the heteropoly compounds are structurally stable.

For the physical mixtures of $Cs_{2.5}$/1.5%Au/TiO_2 the XRD patterns before (dried) and after catalytic reaction are shown in Fig. 6. The main diffraction lines correspond to the TiO_2,

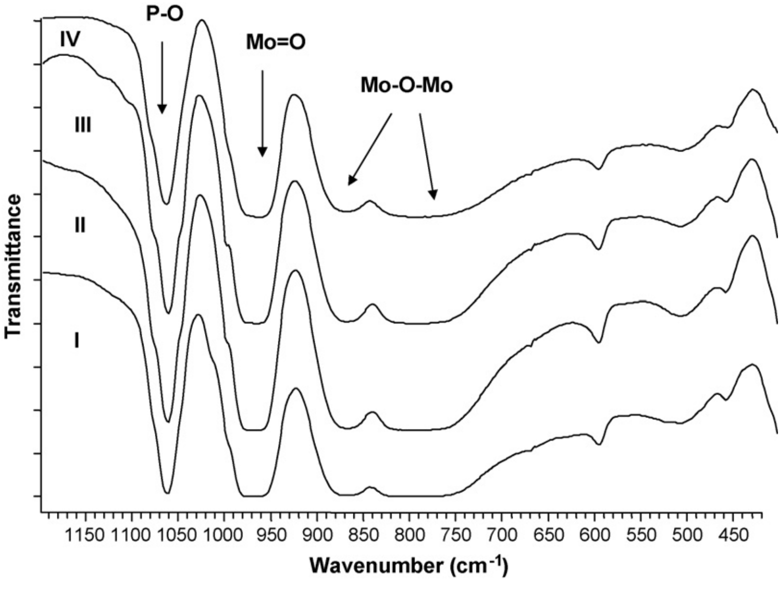

Fig. 1. FT-IR spectra of $H_4PVMo_{11}O_{40}$ (I), $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (II), 1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (Impr.) (III), 1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (sol) (IV), before catalytic reaction.

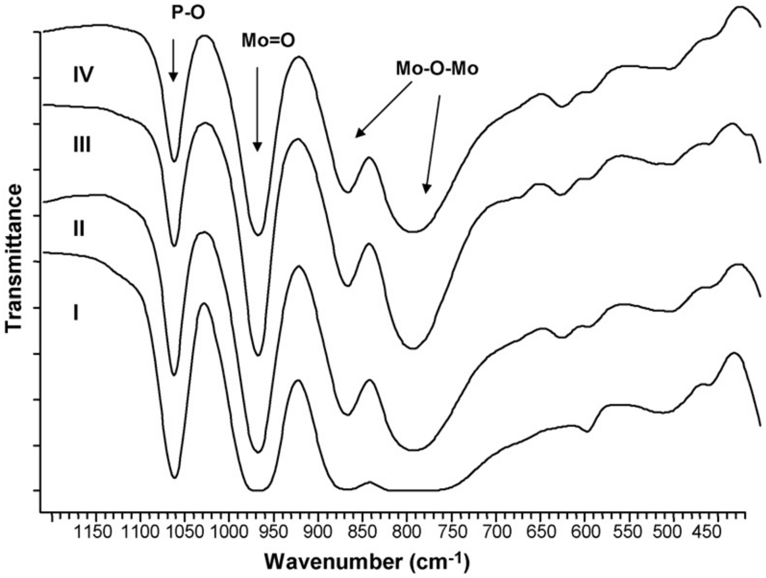

Fig. 2. FT-IR spectra of $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (I), 1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (Impr., O_2/N_2) (II), 1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (Impr., H_2) (III), 1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (sol) (IV), after catalytic reaction.

Table 1
IR data in cm^{-1} for the heteropoly compounds as synthesized

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}
$H_4PVMo_{11}O_{40}$	1063	963	868	793
$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$	1062	968	866	795
1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (Impr.)	1062	968	867	797
1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (sol)	1063	967	868	797

whereas some lines correspond to the HPA crystal phase. After catalytic reaction there was no change in the XRD patterns.

3.1.3. XPS

The XPS technique was used to characterize the $Cs_{2.5}$ salts in the presence of gold. The XPS data for the fresh and used $Cs_{2.5}$ salts are shown in Table 3. For the1%Au/$Cs_{2.5}$ synthesized by the impregnation method (A′), the Mo 3d5/2 peak is in the range of 237.7–237.8 eV and this value can be assigned in the +6 oxidation state. The O 1s peak was in the range of 530.5–531.7 eV and further deconvolution of this peak showed the presence of two states of 530.5 and 531.7 eV. In the case of the fresh sample of 1%Au/$Cs_{2.5}$ synthesized by sol method (C), two states of Mo were observed, one at 232.7 eV and the other at 231.7 eV. The latter can be ascribed to the reduced oxidation state +5 of Mo. This reduction could be due to a small amount of the reducing agent used for the reduction of Au ($NaBH_4$). The binding energy of Mo for the used samples was similar as in the case of the fresh samples, while the BE of O was different. An additional undetermined peak at 532.3 eV was found. These results are in agreement with the IR and XRD data confirming that addition of gold did not modify the Keggin structure. Determination of Au presence and moreover of the oxidation state was not possible either due to the low content of gold which was below detection limits or to the possibility that Au particles lay deeper in the heteropolyacid salt.

In the case of the physical mixtures of $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$/1.5%Au/$TiO_2$ the presence of Au was clear before and after catalytic reaction (Fig. 7). In both cases, the presence of Au in a metallic state was evident.

3.1.4. TPR analysis

TPR analysis of the 1.5%Au/TiO_2 and the $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$/1.5%Au/$TiO_2$ dried samples was performed.

Table 2
IR data in cm^{-1} for the heteropoly compounds after 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}
$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$	1059	966	867	792
1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (Impr.-O_2/N_2)	1063	968	868	794
1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (Impr.-H_2)	1063	968	868	792
1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (sol)	1062	967	868	797

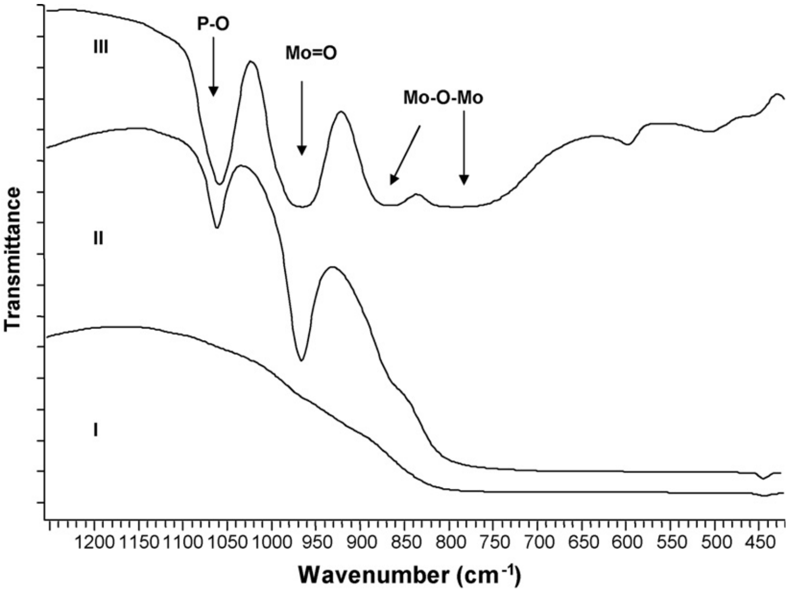

Fig. 3. FT-IR spectra of 1.5%Au/TiO$_2$ (I), $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$/1.5%Au/TiO$_2$ (II), $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (III), before catalytic reaction.

Fig. 8 shows the H_2-TPR profiles of the $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ and $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$/1.5%Au/TiO$_2$ dried samples. Both of the samples showed the onset of reduction peak within the temperature range of 200–240 °C. Reduction was not completed up to 500 °C.

The $Cs_{2.5}$ salt of molybdophosphoric acid decomposition is reported to occur above 540 °C [22,53], but in our case the reduction starts at lower temperatures. According to previously reported data on similar systems [49] the reduction peaks below 540 °C can be ascribed to the partial reduction of transition metal cations in the framework structure of heteropolyacids whereas the reduction of free metal oxides originating from the decomposition of Keggin oxoanion gives reduction peaks above 540 °C. Any effect of gold on titania on reducibility of heteropolyacid, if present, is not readily apparent in the temperature range considered in this study.

3.2. Catalytic activity

3.2.1. Unsupported heteropolyacid catalysts

The catalytic activities on unpromoted and gold-promoted heteropolyacid catalysts are presented in Table 4. Whereas the unsubstituted $H_4PVMo_{11}O_{40}$ resulted unstable and decomposed partially into the mixture of the constituting oxides, thus avoiding the evaluation of its catalytic behaviour, the Cs derivative resulted stable up to 8 h on stream, showing high activity and thermal stability either in the absence or in the presence of added gold. In the temperature range of 260–

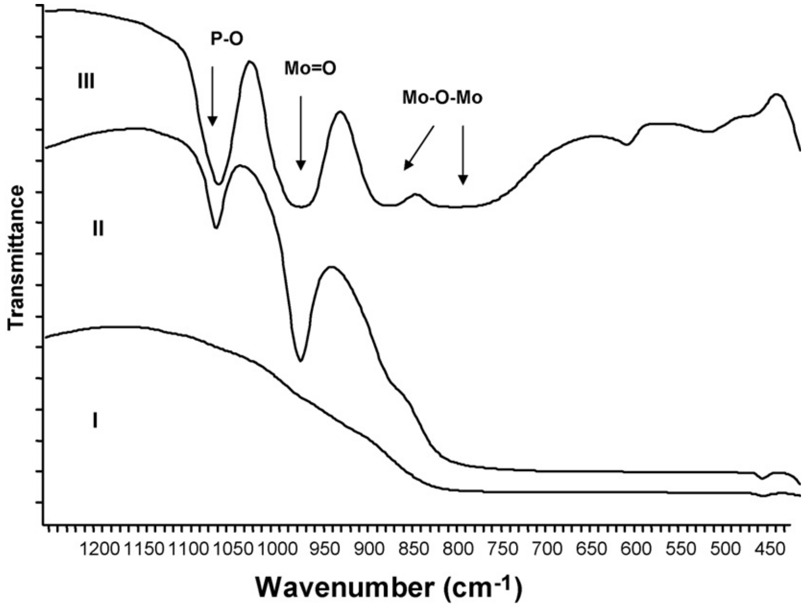

Fig. 4. FT-IR spectra of 1.5%Au/TiO$_2$ (I), $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$/1.5%Au/TiO$_2$ (II), $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (III), after catalytic reaction.

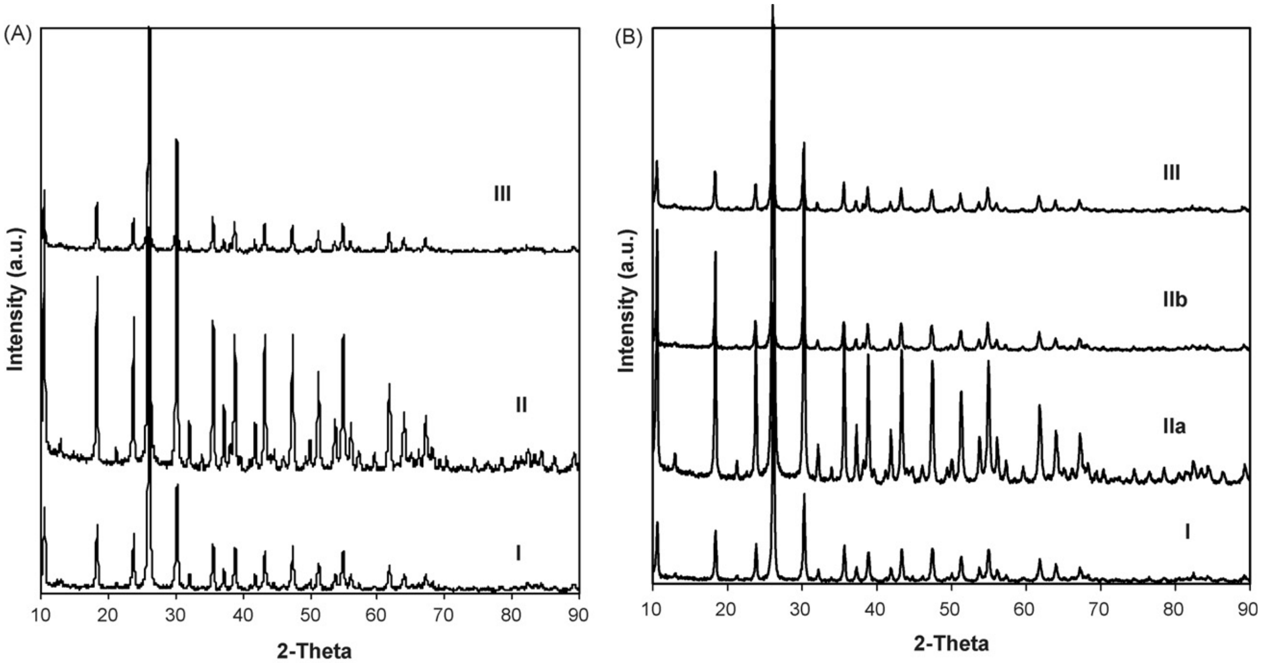

Fig. 5. X-ray diffraction patterns of the samples (A) before and (B) after reaction, $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (I), 1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (Impr.) (II), 1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (Impr.-O_2/N_2) (IIa), 1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (Impr.-H_2) (IIb), 1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (sol) (III).

300 °C, a strong effect of heat pre-treatment conditions on catalytic performance was observed for the unpromoted $Cs_{2.5}$ salt (Table 4, entries 1 and 3). Heat pre-treatment under N_2/O_2 (indicated as method A) resulted in a more active and selective catalyst towards acetic and acrylic acids with respect to heat pre-treatment under H_2 (indicated as method B). Moreover, the loss in the selectivity to oxygenated products was at the benefit of CO_2. As it can be seen, the heat pre-treatment of $Cs_{2.5}$ by method A allowed also the best conversion (36.1%) and selectivity to acrylic acid (7.5%) being acetic acid a second valuable by-product (34.7%) (Table 4, entry 1). Gold addition to $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ samples did not result in any structural changes as we discussed in section 3.1. However, is worth wise to note the catalytic performance of the $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ catalysts promoted with Au under different preparation methods and heat pre-treatment conditions. In particular, we outline the following points:

Sol preparation method (method C) produced 1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ catalyst that was able to induce the total oxidation of propylene (Table 4, entries 8 and 9) with selectivity to CO_2 reaching 90% even at low level of conversion (4–16%). According to previous work, we have shown [50] that the

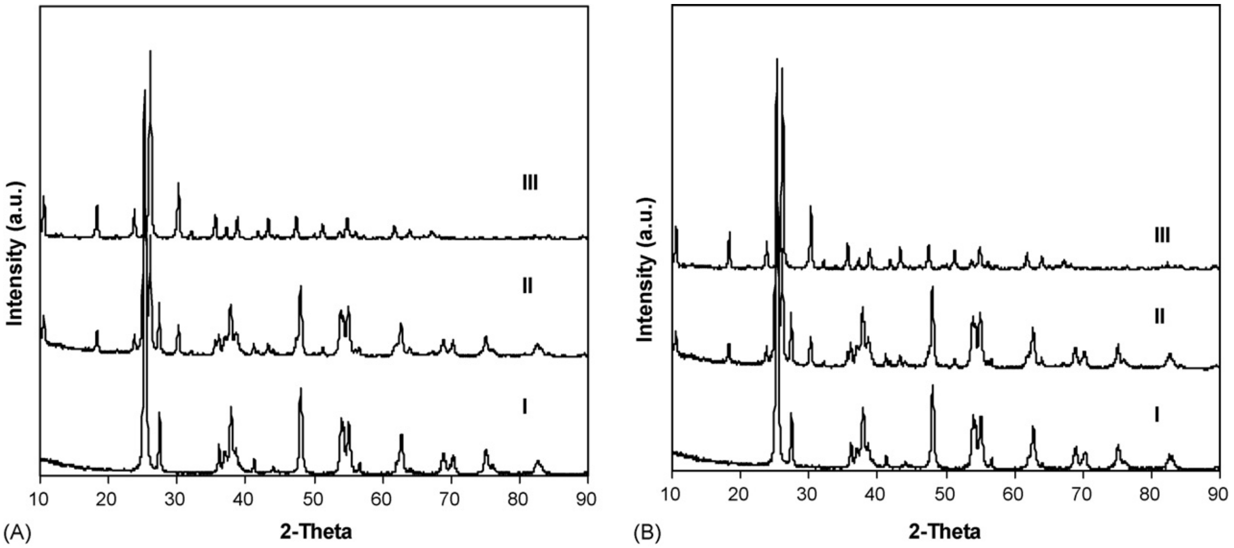

Fig. 6. X-Ray diffraction patterns of the samples (A) before and (B) after reaction, 1.5%Au/TiO_2 (I), $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$/1.5%Au/$TiO_2$ (II), $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (III).

Table 3
Binding energies of 1%Au/$Cs_{2.5}$ and 1.5%Au/TiO_2 + $Cs_{2.5}$ heteropoly compounds by XPS

Catalyst	Before reaction			After reaction		
	Mo $3d_{5/2}$ (eV) (% relative intensity)	O 1s (eV)	Au $4f_{7/2}$ (eV)	Mo $3d_{5/2}$ (eV)	O 1s (eV)	Au $4f_{7/2}$ (eV)
1%Au/$Cs_{2.5}$ (Impr.)	232.8 (100)	530.5 (81.2) 531.7 (18.8)	–	232.7 (100)	530.4 (74.3) 531.6 (17.6) 532.3 (8.1)	–
1%Au/$Cs_{2.5}$ (sol)	–	–	–	232.7 (95.6) 231.7 (4.4)	530.4 (81.4) 531.6 (18.6)	–
1.5%Au/TiO_2		530.0 (79.6) 530.9 (8.7) 531.2 (11.7)	83.7 (100)		529.9 (89.2) 531.6 (10.8)	83.7 (100)
1%Au/TiO_2 + $Cs_{2.5}$	230.8 (19.3) 232.1 (80.7)	528.9 (18.5) 530.1 (68.1)	83.7 (100)	232.5 (100)	529.8 (74.9) 530.6 (16.4) 531.5 (8.7)	83.9 (100)

corresponding sol preparation method can form particles with particle size ranged between 4 and 6 nm. These particles can be the active sites for promoting the total oxidation. On the other hand, impregnation method gave better catalytic performance with respect to the sol preparation method not only in terms of conversion (33–32% for impregnation method versus 17% for sol preparation method at the same reaction temperature (Table 4, entries 5, 7 and 9), but mainly in terms of selectivity to acrylic acid (4–5% for impregnation method A′, B′ versus 0.5% for sol preparation method C). The observed lower level of conversion with sol preparation method with respect to the impregnation method could be due to the presence of PVA (protective layer) or boron derivatives formed during the reduction step generating a poisoning effect on active sites responsible for converting propylene.

In the case of the impregnation method, two different approaches (depending on the heat pre-treatment conditions) were applied in order to reduce gold. In the first case, the heat pre-treatment was performed under N_2/O_2 conditions (indicated as method A′) and in the second case under H_2 flow (indicated as method B′) and in both cases the heat pre-treatment temperature was at 300 °C. Comparison of the catalytic data on these two different heat pre-treatment methods showed a rather complicated picture. At low reaction temperature (260 °C), heat pre-treatment under N_2/O_2 resulted in a significant formation of oxygenated products, especially in the formation of acrolein, whereas under H_2 treatment resulted in a significant amount in the CO_2 formation at the expense of acrolein mainly (Table 4, entries 4 and 6). At higher temperature (300 °C), the formation of acrolein was diminished, whereas significant increase in the formation of CO_2 was observed for the former case (treatment under N_2/O_2). In the latter case (treatment under H_2), significant formation of acetic and acrylic acids was observed (Table 4, entries 5 and 7). In both treatment procedures, conversion was similar at the same reaction temperature. In order to evaluate the effect of heat pre-treatment method (N_2/O_2 versus H_2), comparison with the catalytic performance of the unpromoted $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ catalysts at the same treatment conditions is essential. In the case of treatment under N_2/O_2, similar conversion levels were

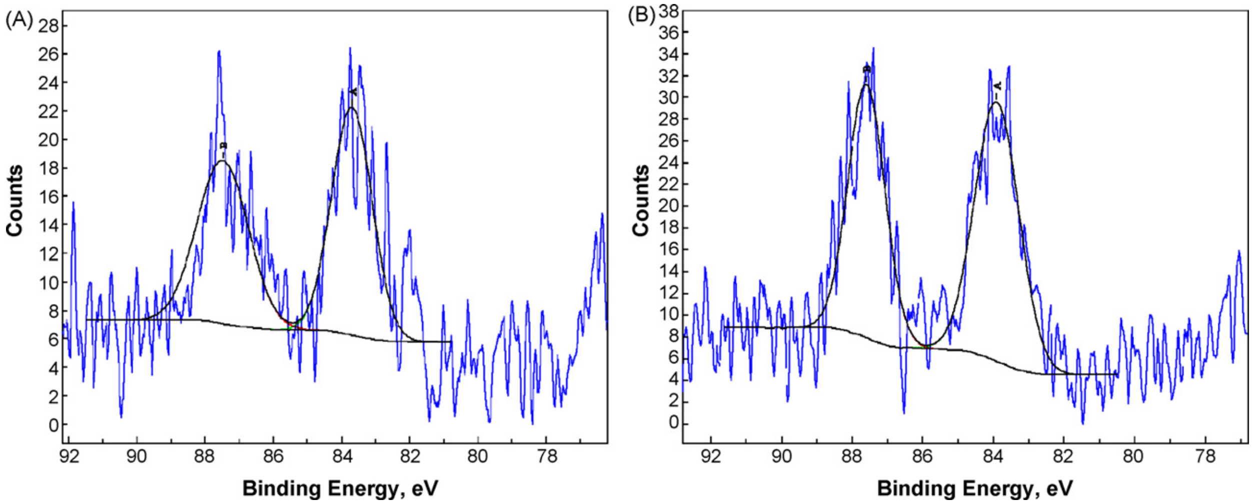

Fig. 7. XPS spectrum of the Au 4f region of $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$/1.5%Au/$TiO_2$ before catalytic reaction and after catalytic reaction (A and B, respectively). Au $4f_{7/2 \text{ and } 5/2}$ doublets (A and B) showed the presence of Au(0), continuous line.

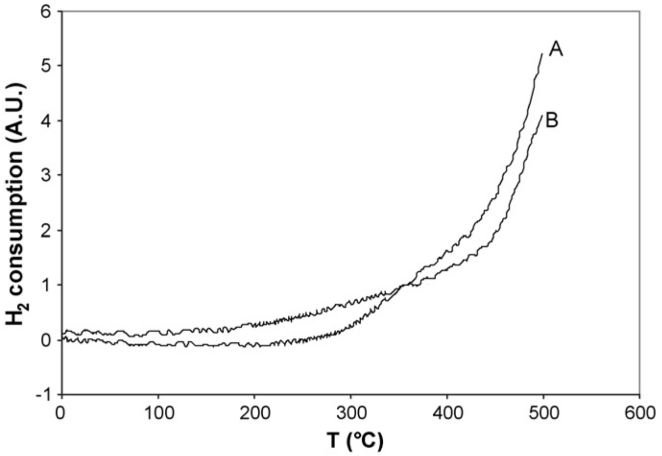

Fig. 8. Temperature-programmed reduction (H_2-TPR) profiles of the $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (A) and $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$/1.5%Au/$TiO_2$ (B) samples.

observed for both catalysts (unpromoted and gold promoted heteropolyacids). However, a different distribution of products was found. The unpromoted $Cs_{2.5}H_{1.5}PVMo_{11}O_{4n0}$ catalyst gave higher selectivity to acetic and acrylic acids (Table 4, entries 1 and 5) with respect to the modified 1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ catalyst. The decrease of acetic and acrylic acids with the modified 1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ catalyst was at the benefit of CO_2. The treatment under H_2 flow (Table 4, entries 3 and 7), resulted in a slight improvement in the formation of oxygenated products for the promoted 1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ catalyst (35.4% selectivity towards acetic and acrylic acids) with respect to the unpromoted $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (29.6% selectivity towards acetic and acrylic acids), whereas activity was slightly enhanced. Nevertheless, treatment under H_2 flow seems to be a less effective method for the formation of oxygenated products, since a higher formation of CO_2 was observed. As we mentioned above, the addition of gold did not result in any structural change of the Keggin anion or in the electronic state of molybdenum when the impregnation method was used. Moreover, as it has been previously reported [51], Au addition enhanced the reducibility of the metal components (Mo and V) as it was shown by TPR analysis, which, however, could not be confirmed by XPS analysis. Treatment under H_2 lead to slightly reduced Mo and V species, which can be responsible for the formation of electrophilic oxygen species. This will result in the promotion of the unselective oxidation to CO_2 by cleavage of the C–C bond. In addition, Au can have an active role in the promotion of the reducibility of the Mo and V species by activation of H_2. The formed H_2 atoms will migrate onto the Mo and V surface with a consequence further reduction of these species, as it has been proposed.

The effect of water concentration was studied for the 1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$-A′ catalyst (Table 5). It is well known that introduction of water in the feed has a beneficial role in the formation of oxygenated products depending on its concentration [52]. In our studies, we varied the concentration of water in the range 8–35% in order to study the effect of water. As it can be seen from the catalytic data (Table 5) by increasing water concentration, a decrease in conversion was observed, whereas selectivities to oxygenated products diminished significantly. These results show that concentration of water affects significantly the distribution of products [54].

Based on the above results, we can indicate that the heat pretreatment procedure is influencing appreciably the distribution of the products, with pre-treatment procedure under N_2/O_2 flow to improve the selectivity of the oxygenated products for the 1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ catalyst.

3.2.2. $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ supported on 1.5%Au/TiO_2

Using a support carrier for depositing metal components is a typical method employed in the industry and in the academia, due to the high thermal stability, surface area and oxygen storage of the support used. Thus, we thought to deposit $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ onto preformed gold particles on TiO_2. In this way, elements which were too expensive to be used as bulk oxide catalysts could be economic as much smaller amounts will be needed for creating a support phase. Catalytic data are illustrated in Table 6. High activity but poor selectivity to acrylic acid was obtained with the unsupported 1.5%Au/TiO_2. The major product was CO_2, indicating that the promotion of the total oxidation was favoured, as it is expected. This result can be due to the effect of gold particle

Table 4
Comparison of HPA and HPA with Au modified catalysts

Entry	Catalyst	[a]vol.%	T (°C)	Conversion (%)	Selectivity (%)						Yield
					CO_2	[b]ACT	[b]ACR	[b]Ac.A.	[b]A.A.	[b]ΣO.P.	[b]A.A.
1	$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$-A	22.0/11.0/31.8/35.2	300	36.1	47.8	0.6	0.5	34.7	7.5	43.3	2.7
2	$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ -B	22.0/11.0/31.8/35.2	260	29.6	51.6	0.5	0.0	33.1	2.3	35.9	0.7
3	$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ -B	22.0/11.0/31.8/35.2	300	27.3	62.9	0.9	0.7	25.8	3.8	31.2	1.0
4	1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$-A′	22.0/11.0/31.8/35.2	260	29.4	31.9	3.3	14.3	16.9	3.8	38.3	1.1
5	1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$-A′	22.0/11.0/31.8/35.2	300	33.0	63.1	2.5	1.1	20.9	4.1	28.6	1.4
6	1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$-B′	22.0/11.0/31.8/35.2	260	28.0	72.1	0.0	0.0	21.3	1.0	22.3	0.3
7	1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$-B′	22.0/11.0/31.8/35.2	300	32.2	56.8	1.0	0.2	31.2	4.6	37.0	1.5
8	1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$-C	22.0/11.0/31.8/35.2	260	3.9	90.2	0.0	0.0	4.7	0.6	5.3	0.02
9	1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$-C	22.0/11.0/31.8/35.2	300	16.5	91.6	0.2	0.0	6.0	0.5	6.7	0.1

[a] Propylene:oxygen:nitrogen:water.

[b] ACR, acrolein; ACT, acetone; Ac.A., acetic acid; A.A., acrylic acid; ΣO.P., sum of oxygenated products (ACR, ACT, Ac.A. and A.A.).

Table 5
Catalytic data of 1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$-A′ for propylene oxidation at different H_2O concentration

Entry	Catalyst	[a]vol.%	T (°C)	Convversion (%)	Selectivity (%)						Yield
					CO_2	[b]ACT	[b]ACR	[b]Ac. A.	[b]A.A.	[b]ΣO.P.	[b]A.A.
1	1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$-A′	31.2/15.6/45.0/8.2	300	42.1	24.2	0.7	0.4	50.5	9.0	60.6	3.8
2	1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$-A′	26.7/13.4/38.6/21.3	300	40.9	31.8	2.7	1.5	41.8	7.6	53.6	3.1
3	1%Au/$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$-A′	22.0/11.0/31.8/35.2	300	33.0	63.1	2.5	1.1	20.9	4.1	28.6	1.4

[a] Propylene:oxygen:nitrogen:water.
[b] ACR, acrolein; ACT, acetone; Ac.A., acetic acid; A.A., acrylic acid; ΣO.P., sum of oxygenated products (ACR, ACT, Ac.A. and A.A.).

Table 6
Comparison of 1.5%Au/TiO_2 and 1.5%TiO_2 modified with HPA catalysts

Entry	Catalyst	[a]vol.%	T (°C)	Conversion (%)	Selectivity (%)						Yield
					CO_2	[b]ACT	[b]ACR	[b]Ac.A.	[b]A.A.	[b]ΣO.P.	[b]A.A.
1	1.5%Au/TiO_2	31.2/15.6/45.0/8.2	260	39.3	57.8	1.9	0.8	25.8	4.5	33.0	1.8
2	1.5%Au/TiO_2	31.2/15.6/45.0/8.2	300	35.8	66.2	2.3	4.6	22.9	1.1	30.9	0.4
3	1.5%Au/TiO_2/HPA	31.2/15.6/45.0/8.2	260	35.3	37.9	4.1	18.9	31.2	2.4	56.6	0.9
4	1.5%Au/TiO_2/HPA	31.2/15.6/45.0/8.2	300	38.2	29.3	0.5	14.5	45.9	3.0	63.9	1.2
5	1.5%Au/TiO_2/HPA	15.6/31.2/45.0/8.2	300	75.7	78.5	1.2	1.2	17.7	0.2	20.3	0.2
6	$Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$-A	31.2/15.6/45.0/8.2	300	46.1	13.5	0.2	0.4	61.7	12.3	74.6	5.6

[a] Propylene:oxygen:nitrogen:water.
[b] ACR, acrolein; ACT, acetone; Ac.A., acetic acid; A.A., acrylic acid; ΣO.P., sum of oxygenated products (ACR, ACT, Ac.A. and A.A.).

size and in addition to the TiO_2 support, as it has been observed by Gasior et al. [41].

Supporting $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ on the 1.5%Au/TiO_2 improved considerably the catalytic performance of the 1.5%Au/TiO_2 with respect to the formation of oxygenated products which raised from 30.9 to 63.9% (Table 6, entries 2 and 4), whereas the formation of CO_2 was substantially reduced, indicating that the active sites responsible for the total oxidation were suppressed. More in particular, selectivity to acetic acid doubled owing to addition of $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$. This result can be explained due to the increased Brønsted acidity that $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ salt possesses. In fact, a comparison with the unpromoted $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ (Table 6, entry 6) showed that the significant increase in oxygenated products is mainly due to the presence of $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ which induced the high conversion to acetic and acrylic acids (Table 6, entries 4 and 6). However, acrolein formation up to 14.5% selectivity at 300 °C was improved using the mixed $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$-1.5%Au/$TiO_2$ catalytic system with respect to both separated catalysts (Table 6, entries 2, 4 and 6). A similar synergistic effect could be considered also at 260 °C, producing the highest observed selectivity towards acrolein formation (18.9%, entry 3). Also previous investigations proved that the enhancement of acetic acid at the expense of acrylic acid was related to the presence of strong Brønsted sites [21,52]. Similar conversion levels were obtained in both cases. Changing reaction conditions from propylene-rich to propylene-lean affected considerably the conversion and the distribution of the products for the supported $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$/1.5%Au/$TiO_2$. Thus, an increase of conversion with substantially loss in the formation of oxygenated products was observed at the benefit of CO_2 product (Table 6, entries 4 and 5).

4. Conclusions

The present study has shown that the method of deposition of Au onto $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ affects significantly the activity and distribution of products, either by enhancing the total combustion or by improving the formation of oxygenated products, especially acetic acid. Heat pretreatment procedure shows to be important in the impregnation method according to a complex pattern. Activation of the Au modified catalysts under H_2 flow gave slightly higher selectivity to oxygenated products rather than under O_2/N_2 flow at higher reaction temperature (e.g. 300 °C), whereas at lower temperature a significant increment in the formation of oxygenated products under N_2/O_2 heat pre-treatment with respect to H_2 treatment was observed. Nevertheless, heat pretreatment under H_2 flow resulted in general in a higher level of CO_2 formation, indicating that the referred heat pretreatment procedure seems to be a less effective method for the formation of oxygenated products. In the case of sol immobilization method, the promotion of the total oxidation was observed.

Owing to the intrinsic selectivity towards oxygenates of $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$, deposition of this latter on 1.5%Au/TiO_2 improved remarkably the behaviour of the catalytic system: CO_2 was significantly diminished, probably due to the blockage of active sites responsible for the total oxidation, whereas acrolein production was increased in a synergistic manner. Therefore, we feel that by depositing small amounts of $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ on the preformed Au/TiO_2 and balancing the effect of both components under appropriate reaction conditions, we should be able to direct the propene oxidation towards oxygenated in a more selective way.

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