



## Specific insight of active sites in $\text{Cs}_2\text{Te}_x\text{V}_y\text{PMo}_{12}\text{O}_{40}$ catalysts efficient for selective oxidation of isobutane by operando resonance Raman spectroscopy

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### ABSTRACT

Keggin-type phosphomolybdates with cesium, tellurium and vanadium as counter-cations, recently shown to be efficient for selective oxidation of isobutane, were characterized by diffuse reflectance and Raman spectroscopy. In the present study, it was shown that the Raman bands appearing in addition to those of  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  in these catalysts after reaction were observed with much better sensitivity using exciting lines at 647.1 and 785 nm. This phenomenon, linked to the existence of d–d transitions and intervalence charge transfers at 680 and 860 nm, respectively, arises mainly from reduction of the probed depth and to a lesser extent, from enhancement effect using resonance Raman spectroscopy. The better sensitivity of this technique was used to follow specifically the additional bands before, during and after reaction. They were attributed to highly reduced phosphomolybdates stabilized under reaction mixture and possibly capped by  $\text{Te}^{4+}$  and  $(\text{V}=\text{O})^{2+}$ . The reduced species would be present in a layer lying over unreduced Keggin salt and specifically probed using resonance Raman spectroscopy. Substitution by tellurium cations was shown to favour reduction of Keggin heteropolyanions under reaction mixture. Operando resonance Raman experiments evidenced that, for the samples without vanadium, reduced phosphomolybdates were formed above 120 °C during the raise up to the reaction temperature whereas for the samples with vanadium, small amount of these species was already observed before reaction because of oxidation of  $\text{V}^{3+}$  to  $\text{V}^{4+}$  cations during drying. This amount also increased during the thermal activation under reaction feed. The relative intensity of the additional bands was maximal when the catalysts were active and selective under reaction mixture. After reaction, this parameter was related to the selectivity to methacrolein and methacrylic acid suggesting that reduced phosphomolybdates are more selective active sites.

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### 1. Introduction

The operando methodology is powerful to establish relationships between catalytic activity and catalyst structure by coupling characterization experiments and catalytic measurements in a same cell. It is a tool to design and prepare better catalysts [1–3]. However, in heterogeneous catalysis, it is sometimes difficult to identify active sites because they are located at the surface of catalysts and can be present in very limited number. Therefore, well-chosen techniques are required to determine the structure of these sites. Resonance Raman spectroscopy allows observation of diluted chromophores enhancing bands of molecules or crystals owning electronic transition in the UV–near IR range when the wavelength of the laser exciting line coincides with that of the transition. Additionally, resonance Raman spectroscopy probes

much less layers of matter than other bulk techniques since the resonance process is often associated with strong (re)-absorption [4,5]. Therefore, it can be key technique to characterize catalytic active sites as previously illustrated in the literature [6–10].

Recently, new catalysts based on phosphomolybdic acid substituted by cesium, tellurium and vanadium cations were shown to be efficient and stable for selective oxidation of isobutane to methacrylic acid [11]. This direct reaction is particularly attractive to replace the current “acetone–cyanohydrin” process that generates numerous toxic wastes [12]. Incorporation of tellurium led to improved selectivity to methacrylic acid and incorporation of vanadium to improved catalytic activity [13].

The catalysts had been characterized by various bulk techniques before and after reaction revealing limited features. Indeed, XRD patterns only revealed a cubic structure typical of cesium heteropolysalt and IR spectra only contained vibration bands typical of  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  Keggin anions. However, X-absorption spectroscopies were much more informative since the oxidation state of both tellurium and vanadium was determined to be IV

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before and after reaction and the presence of [TeO<sub>4</sub>] clusters capping Keggin anions has been proposed [13]. Raman spectra of the catalysts achieved before reaction with exciting line at 514.5 nm were typical of Keggin units with cesium as counter-cations [14]. However, small additional bands were evidenced after reaction for the best compounds [13]. These bands cannot be attributed to any allotropic form of MoO<sub>3</sub> nor to fragments of Keggin units as previously described [15].

In this paper, enhancement of additional bands by resonance effect has been evidenced using exciting lines at 647.1 and 785 nm. The use of resonance Raman spectroscopy allowed specific insight of the corresponding species thanks to much better sensitivity. From visible diffuse reflectance spectra, this better sensitivity was explained at first by strong re-absorption using red or near IR exciting line and to a lesser extent by resonance effect. It allowed a more precise comparison of additional bands with reference spectra for attribution, to investigate the influence of the counter-cations composition on their intensity and to establish relationships with catalytic properties. The formation of the corresponding species and their stability depending on the redox strength of the atmosphere were investigated achieving in situ and operando measurements.

## 2. Experimental

### 2.1. Preparation of the Cs<sub>2</sub>Te<sub>x</sub>V<sub>y</sub> catalysts and references

The catalysts were prepared substituting protons contained in phosphomolybdic acid by cesium, tellurium and vanadium cations [13] and were labelled according to their atomic counter-cations content (Cs<sub>2</sub>Te<sub>x</sub>V<sub>y</sub>). During typical preparation, 8.16 g of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>·xH<sub>2</sub>O (Fluka, Ref. 79560) and various amounts of telluric acid were dissolved in 140 ml of deionised water. A second solution containing 1.3 g of Cs<sub>2</sub>CO<sub>3</sub> in 0.4 ml of deionised water was added dropwise leading to the formation of a precipitate. The mixture was kept under stirring for 1 h at 80 °C before evaporation at reduced pressure using a rotavapor, was then dried at 125 °C and finally calcined under air flow at 360 °C for 6 h. The preparation of Cs<sub>2</sub>Te<sub>x</sub> samples was achieved at this step. To obtain the Cs<sub>2</sub>Te<sub>x</sub>V<sub>y</sub> samples, remaining protons were substituted by maintaining Cs<sub>2</sub>Te<sub>x</sub> salts in a solution of toluene containing vanadium acetylacetonate for 6 h under stirring at room temperature. Finally, the substituted solids were only dried under reduced pressure at 60 °C using a rotavapor. For testing measurements, the Cs<sub>2</sub>Te<sub>x</sub>V<sub>y</sub> samples were directly heated under reaction mixture.

(MoO<sub>2</sub>)<sub>0.5</sub>(PMo<sub>14</sub>O<sub>42</sub>) reference compound was obtained according to a procedure published by Marosi et al. [16,17] calcining the (NH<sub>4</sub>)<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>·xH<sub>2</sub>O ammonium salt (Aldrich, Ref. 342165) under N<sub>2</sub> flow at 470 °C for 6 h. The XRD pattern of the prepared compounds was completely indexed with that of (MoO<sub>2</sub>)<sub>0.5</sub>(PMo<sub>14</sub>O<sub>42</sub>) (PDF-ICDD 056-0165). IR vibration bands of this sample were located at 1057, 1052, 1009, 994, 972, 961, 866, 786, 768, 715, 675, 579, 550, 534, 508, 466, 451, 440 and 423 cm<sup>-1</sup>. Four electron reduced (TBA)<sub>7</sub>PMo<sub>12</sub>O<sub>40</sub> salt was also prepared by reduction of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> (Fluka, Ref. 79560) using N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (Aldrich, Ref. 207942) in 50% dioxane–50% water solution followed by precipitation using TBABr salt (Fluka, Ref. 86857). The sample evidenced <sup>31</sup>P-NMR band at –13.3 ppm typical of β-IV reduced Keggin anion [18].

### 2.2. Characterization techniques

Raman experiments were achieved using UV–vis–NIR Lab-Ram HR spectrometer (Horiba–Jobin Yvon) equipped with BFXM confocal microscope, interference and Notch filters and CCD

detector cooled at –76 °C by Peltier effect. The diffused light was spatially dispersed with a 1800 grooves/mm or a 300 grooves/mm diffraction grating. The influence of the laser wavelength on the Raman spectra of catalysts has been investigated. For that purpose, the exciting lines at 457.9, 514.5 and 647.1 nm delivered by a 2018 RM Ar–Kr laser (Spectra physics) and the exciting line at 785 nm obtained from a diode laser were used. After evidencing resonance effect of additional bands both at 647.1 and 785 nm, the first one was preferred to the second one because black body emission is intense in near IR range even at moderate temperature and can limit in situ and operando experiments.

For all the exciting lines, an extreme care has been taken to choose a working laser power for which the heating effect was negligible. Therefore, the power at the samples was limited to only 100 μW for all the experiments. In that regard, it is important to mention that the enhancement of additional bands cannot be observed in ambient air using a too much high laser power because of the heating of samples.

An objective with magnification 100× was selected for ex situ measurements whereas a long working distance objective with magnification 50× was used for in situ and operando studies. During ex situ measurements, several areas were analysed under microscope for each composition. The comparison of spectra from one point to the other has shown good homogeneity of the catalysts before and after reaction.

In situ Raman spectra were recorded during thermal treatments of samples located in a crucible lying on the heating sole of a THMS600 cell linked a TMS94 programmer (Linkam). The set-up for operando experiments was previously described in detail [19]. It consists of a home-made furnace containing four heating plugs and fixed-bed quartz micro-reactor specially designed for such measurements. The last one contained a quartz window for light transmission, thermocouple hollow, inlet–outlet gas connections and a porous disc on which the investigated catalysts laid. The feedstock composition used for operando experiments was 27% iC<sub>4</sub>H<sub>10</sub>/13.5O<sub>2</sub>/10H<sub>2</sub>O/49.5He and corresponded to an optimised mixture [13]. The temperature was varied from 20 °C up to 376 °C under a 20 ml min<sup>-1</sup> gas flow at atmospheric pressure. iC<sub>4</sub>H<sub>10</sub> and O<sub>2</sub> conversions were determined using a VG ProLab mass spectrometer (Thermo Electron Corporation) located after the cell. Selectivities to methacrolein (MA) and methacrylic acid (MAA) products were obtained from gas chromatography analysis using a GC 2012 (Shimadzu) after ice-cooled trapping. They were calculated from the formula  $S_i = n_i / \Delta n i C_4 H_{10}$  where  $S_i$  is the selectivity to MA or MAA,  $n_i$  the number of moles produced during the time of trapping and  $\Delta n i C_4 H_{10}$  the number of moles of isobutane converted at the same time. CO and CO<sub>2</sub> products were detected with the mass spectrometer but not quantified. Traces of acetic acid were also formed during operando experiments.

Diffuse reflectance spectra were carried out on powders in the visible–near IR range using a Lambda 35 spectrometer (PerkinElmer) equipped with integrating sphere. A Spectral<sup>®</sup> standard sample was used as reference. The spectra are reported using the Kubelka–Munk function given by  $FR(\lambda) = (1 - R(\lambda))^2 / 2R(\lambda)$  where  $R(\lambda)$  corresponds to the reflectance at the  $\lambda$  wavelength.

Chemical analysis of Mo, V, Te and P cations was obtained by atomic emission using an induced plasma technique and using an air–acetylene flame for Cs cations. X-ray diffraction patterns were achieved from 3° to 80° (2θ) with a step of 0.02° using a Siemens D5005 diffractometer and Cu Kα radiation. The ICDD database was used for indexing. Transmission FTIR spectra of samples dispersed in KBr were recorded with a Brüker Vector 22 spectrometer. Finally, <sup>31</sup>P-NMR spectra were acquired on a Bruker DSX 400 spectrometer.

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