



Raman monitoring of a catalytic system at work: Influence of the reactant on the sensitivity to laser-induced heating



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ABSTRACT

Characterizing catalysts under working conditions is crucial to understand and to optimize their behavior and performance. However, when Raman spectroscopy is used, attention has to be paid to laser-induced artefacts. While laser irradiation is often claimed to lead to a temperature gradient between the integral catalyst bed and the sampling point, neither the circumstances when such effect appears, nor if it systematically occurs or not, are really explored in details. The present paper shows that the sensitivity of a catalyst to laser-induced heating largely depends on the gas composition under which the analysis is done, in particular that it depends whether the catalyst has adsorbed reactant molecules or not. These aspects are here addressed via the Raman *in situ* exploration of $\text{H}_3\text{PW}_{12}\text{O}_{40}$. This heteropolyacid is a widely used acid catalyst due to its very high Brønsted acidity, approaching the superacid region. In particular, we have investigated the impact of laser irradiation in the Raman monitoring of solid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ at work under a flow of methanol in nitrogen at 50 °C. When 1 single spectrum of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was measured after 3 h of exposure to methanol, the characteristic C–H vibration bands of adsorbed methanol appeared. However, when spectra were measured continuously throughout the experiment, the same C–H vibration bands were observed only during the first hour, then they disappeared and the characteristic bands of polyaromatic molecules appeared. Under continuous laser irradiation, adsorbed methanol was thus converted into polyaromatic coke as resulting from a laser-induced heating. However, the spectra collected under pure nitrogen show that the laser does not heat the catalyst in the absence of methanol. UV–Vis revealed the reason of the laser-induced heating in the presence of methanol, and the subsequent formation of coke. Actually the catalyst gets reduced by the adsorbed methanol, what darkens the catalyst bed. Such a darkening renders the catalyst sensitive to laser-induced heating, which in turn leads to the formation of coke. Under continuous laser irradiation, methanol thus auto-initiated its own catalytic conversion, finally leading to the deposition of coke. Such artefact must be avoided if one wants to study the true behavior of the catalyst at work. This paper shows that, for reducible samples analyzed in the presence of reductive molecules, this is only possible by shining the laser intermittently and not continuously. More generally, it actually shows that the adequate way to irradiate a catalyst (continuous vs intermittent) in an *in situ/operando* Raman analysis depends on the gas flow composition.

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1. Introduction

Heteropolyacids (HPAs) are metal-oxygen clusters with unique molecular and electronic structural diversity. They are nowadays widely used in both acid and redox catalysis. Indeed, they possess on one hand a very strong Brønsted acidity, approaching the superacid region, and on the other hand interesting redox properties which can be tuned by varying their chemical composition [1,2]. Among the large variety of HPAs, Keggin-structure HPAs are the most studied. Indeed, they are the most thermally stable and the most easily available ones [2,3]. A Keggin unit is composed of a heteropolyanion stabilized by acidic

protons. The heteropolyanion has the formula $[\text{XM}_{12}\text{O}_{40}]^{n-}$, where X is the heteroatom (often P^{5+} , Si^{4+}) and M is the addenda atom (transition metal, typically Mo^{6+} , W^{6+}). Resulting from the condensation of oxoanions, the polyanion is composed of a central XO_4 tetrahedron surrounded by twelve MO_6 octahedra [3,4]. In the hydrated solid, Keggin units are coordinated with crystallisation water molecules. The most common form (stable up to 100 °C) contains six crystallisation water molecules per Keggin unit, forming a body-centered cubic structure with Keggin anions at the lattice points and acidic H_5O_2^+ bridges along the faces [2].

When investigating catalytic processes based on Keggin HPAs, establishing structure–catalytic activity relationships is an important challenge. Indeed, under reaction conditions, the crystallographic structure of Keggin HPAs can change. Depending on the process,

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crystallisation water molecules can be released, and/or defective structures can be formed [5,6]. Relating these possible changes to the catalytic activity in real time is essential to understand as well as possible the HPA's properties and eventually to optimize them. *Operando* characterization is the methodology which can allow achieving this. It has been introduced into the catalysis literature in 2002. It is defined as a “combined spectroscopic measurement and simultaneous online measurement of catalytic activity/selectivity values during catalytic reaction studies” [7]. The term “*operando*”, meaning “operating” in Latin, is justified as the spectra of the catalyst and of the molecules adsorbed on it are measured under true catalytic conditions. Among all the available spectroscopic techniques, Raman spectroscopy is particularly suitable for *operando* investigations as the interference from the gas phase is negligible [7]. Nevertheless, it is very important to carefully investigate potential impacts of laser irradiation on the catalytic process before drawing any conclusion from the spectra. Indeed, there is an issue often claimed by Raman spectroscopists which is laser-induced heating. It is reported to lead to catalyst damage and/or to a temperature gradient between the sampling point and the integral catalyst bed, making the establishment of structure-activity relationships very difficult [8].

We report here on another aspect, more subtle and likely difficult to detect, that is important to consider when shining a laser on a catalyst at work. Precisely, we show how the presence of the reactant molecules influences the sensitivity of the catalyst to laser-induced heating when the system is monitored at work through Raman spectroscopy. In other words, we show that the occurrence of the laser-induced heating depends on the gas compositions under which the sample is spectroscopied. Understanding this is crucial in *in situ/operando* spectroscopy, which basically aims at observing evolutions of spectral signatures of catalysts when submitted to variations of conditions as the composition of their gaseous environment.

This aspect is here illustrated in the reaction of methanol on the bulk $\text{H}_3\text{PW}_{12}\text{O}_{40}$ hexahydrate. Methanol is nowadays an important reactant as its dehydration leads to dimethylether (DME) [9], which is one of the most promising renewable fuels for the future [10,11]. Over $\text{H}_3\text{PW}_{12}\text{O}_{40}$, namely the strongest Keggin acid, the dehydration of methanol can occur at temperatures as low as 25 °C [12]. *Operando* Raman spectroscopy appears particularly attractive in this process as in principle it allows monitoring the formation of coke molecules (carbonaceous deposits), namely the most frequent reason for HPA deactivation [3]. Using the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ – methanol system as a model, the present work shows how a reactant itself can render a catalyst sensitive to laser-induced heating, and so distort the picture of the working system and lead to wrong conclusions about the catalyst's properties. More generally, it shows that the method used in an *in situ/operando* Raman analysis (continuous vs intermittent laser irradiation) can be chosen depending on the gas flow composition.

2. Experimental

2.1. Materials

$\text{H}_3\text{PW}_{12}\text{O}_{40}$ has been purchased from Sigma-Aldrich in the form of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ (reagent grade). The powder has been placed overnight under vacuum (<5000 Pa) at room temperature in order to evacuate physisorbed water. As revealed by a subsequent thermogravimetric analysis, the number of crystallisation water molecules present per Keggin unit (x) was then 5.82, rounded to 6 (thermogravimetric profile supplied in the Supplementary Information file, Fig. S1). For Raman monitoring, the $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ (hereafter HPW12) powder has been sieved within 100–200 μm . Methanol, always carried by nitrogen (Praxair 5.0), has also been purchased from Sigma-Aldrich (anhydrous, 99.8%).

2.2. Spectroscopic Monitoring

The impact of methanol on the sensitivity of HPW12 to laser-induced heating during Raman monitoring has been investigated at 50 °C. Methanol (10 vol.%) was carried by nitrogen. A set-up combining Raman spectroscopy not only with online product analysis but also with UV–Visible spectroscopy has been used. UV–Visible spectroscopy allows interpreting phenomena reflected on the Raman spectra by showing changes in the oxidation state of the HPA's transition metal. The set-up was inspired by [13,14]. The powdered samples have been introduced into a quartz reactor with 2 optical windows which allowed characterizing the working catalyst throughout the reaction. The reactor, connected to a gas distribution and manifold, was positioned in the center of a drilled stainless steel cylinder heated by 4 cartridge heaters inserted around the central hole. The temperature was measured with a K type thermocouple positioned inside the sample bed. A hole drilled horizontally in the cylinder allowed the long focal objective to be focused on the sample in order to irradiate it and to collect its Raman signal. The Raman probe was mounted on an xy table to facilitate forward-backward and left-right movements of the laser beam onto the catalyst. A black box covered the whole setup to avoid disturbances from sunlight when measuring spectra.

The study has been carried out in 4 steps. In a first step, HPW12 has been laser-irradiated continuously for 2.5 h at 50 °C under pure nitrogen. Raman spectra have been measured every 4 min. The aim was to assess the impact of a continuous laser irradiation on HPW12's Keggin structure under inert atmosphere. In a second step, HPW12 has been exposed for 3 h at 50 °C to a flow of nitrogen saturated with 10 vol.% of methanol without being continuously laser-irradiated. One single spectrum has been measured after the 3 h of exposure in order to assess the impact of methanol on HPW12's Raman signal. An UV–Visible spectrum has also been measured after the 3 h of exposure in order to assess whether HPW12 has been reduced due to the flow of methanol. In a third step, HPW12 has been laser-irradiated continuously for 3 h at 50 °C under the same methanol-saturated nitrogen flow as in the second experiment. As in the first step, Raman spectra have been measured every 4 min. The aim was to assess the impact of a continuous laser irradiation under working conditions, by comparing the results to the ones of the 2 previous experiments in which the impacts of 1) continuous laser irradiation and 2) exposure to methanol have been studied independently of each other. As a complement to this third step, HPW12 has been additionally analyzed by UV–Visible spectroscopy for 3 h at 50 °C under the same methanol-saturated nitrogen flow in order to monitor its potential continuous reduction with time on stream. UV–Visible spectra have been measured every 2 min. The equivalent blank test under pure nitrogen has also been performed. Finally, in a fourth step, HPW12 has been monitored upon increasing the reactor temperature from 50 °C to 200 °C (1) under nitrogen saturated with 10 vol.% of methanol and 2) under pure nitrogen. The aim was to determine 1) at which temperature the Raman signal of coke appears on HPW12's spectrum and 2) to which extent the Raman signal of HPW12 is shifted with increasing temperature. Indeed, knowing this would allow evidencing a potential local laser-induced temperature rise during the above described irradiation experiments at 50 °C reactor temperature. The temperature program was: heating HPW12 from 25 °C successively to 50 °C–100 °C–110 °C–120 °C–130 °C–140 °C–150 °C–200 °C at a rate of 1 °C/min and with a dwell time of 1 h at each temperature plateau. To exclude any potential impact of continuous laser irradiation, the sample has in this case been irradiated intermittently: at each temperature plateau, irradiation was switched on every 20 min, and switched off again immediately after the spectrum was measured.

In all experiments, the total inlet gas flow (either pure nitrogen or methanol-saturated nitrogen) was of 30 mL/min. It was always sent to the reactor when the latter was still at room temperature, as soon as the temperature rise to 50 °C was launched. To investigate the impact of continuous laser irradiation, 50 °C has been chosen as working

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