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ABSTRACT

Operando Raman spectroscopy is used here to enlighten crucial and yet unconsidered aspects of the catalytic behavior of Keggin heteropolyacids (HPAs) in the gas phase dehydration of methanol to dimethylether (DME). On one hand, HPAs are since a long time claimed as being able to absorb methanol into their bulk, but on the other hand this feature is not yet really exploited when it comes to develop/use HPA-based catalysts for the methanol-to-DME process. Actually, the conditions in which the bulk is simultaneously accessible and catalytically active are not yet clearly reported. Clarifying this is precisely the aim of our work, for which we have used H3PW12O40 and H4SiW12O40. We precisely operando-follow the νs(W=O) band reflecting whether methanol penetrates or not in the HPAs' bulk. We show that, when the HPAs are used without having been beforehand completely dehydrated, methanol penetrates into their bulk. However, the conversion remains low (<5% at...

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Showcasing research from Prof. Eric M. Gaigneaux’s group at the Université catholique de Louvain, Belgium.

Elucidating and exploiting the chemistry of Keggin heteropolyacids in the methanol-to-DME conversion: enabling the bulk reaction thanks to operando Raman

Our lab uses operando Raman spectroscopy in order to fully exploit the catalytic potential of the bulk of heteropolyacids. Here, by properly adjusting the pre-treatment conditions of Keggin units, we drastically gain performance in the methanol-to-dimethylether process.
Elucidating and exploiting the chemistry of Keggin heteropolyacids in the methanol-to-DME conversion: enabling the bulk reaction thanks to operando Raman†

Josefine Schnee and Eric M. Gaigneaux*

Operando Raman spectroscopy is used here to enlighten crucial and yet unconsidered aspects of the catalytic behavior of Keggin heteropolyacids (HPAs) in the gas phase dehydration of methanol to dimethylether (DME). On one hand, HPAs are since a long time claimed as being able to absorb methanol into their bulk, but on the other hand this feature is not yet really exploited when it comes to develop/use HPA-based catalysts for the methanol-to-DME process. Actually, the conditions in which the bulk is simultaneously accessible and catalytically active are not yet clearly reported. Clarifying this is precisely the aim of our work, for which we have used H₃PW₁₂O₄₀ and H₄SiW₁₂O₄₀. We precisely operando-follow the \( \nu_s(W=O) \) band reflecting whether methanol penetrates or not in the HPAs’ bulk. We show that, when the HPAs are used without having been beforehand completely dehydrated, methanol penetrates into their bulk. However, the conversion remains low (<5% at 150 °C) due to remaining crystallisation water reducing the availability of the active protons within the bulk, so limiting the activation of methanol. A complete dehydration pre-treatment is thus required if one wants to fully benefit of the bulk reactivity. However, we show that this benefit is obtained only if the pre-treatment is done adequately. The most intuitive pre-treatment, namely the HPAs’ dehydration at about 300 °C and then cooling down to the reaction temperature 150 °C at which methanol is fed, is shown to be inefficient. This is due to the inaccessibility of the fully dehydrated bulk to methanol, so limiting the catalytic reaction to only the surface of the HPAs. At the opposite, a pre-treatment sequence consisting of dehydrating at 300 °C, then cooling down to 25 °C, exposing to methanol at this temperature, and then only heating to the reaction temperature, is shown to succeed combining penetration of methanol into the bulk and availability of the active protons. With such sequence, an unprecedented conversion of 40% is obtained thanks to a full exploitation of the HPAs’ bulk. These results show that the HPAs’ bulk can contribute significantly to convert methanol, provided that the catalysts are properly pre-treated.

1. Introduction

Dimethylether (DME), an intermediate for the synthesis of various chemical compounds, attracts more and more attention nowadays within the energy sector as a clean alternative fuel.¹,² DME is even considered by some authors as “the fuel for the 21st century”.³ Indeed, it can be used in diesel trucks, for power generation, in fuel cells and also to replace LPG as cooking gas.²,³ It has a very low climate impact as it is non-toxic, non-corrosive and biodegradable in air; and as its combustion leads to almost no emission of particulates.¹,³

One important route for the synthesis of DME is the gas phase dehydration of methanol over a solid acid catalyst. However, to convert methanol, conventional catalysts such as γ-Al₂O₃ or zeolites require high operation temperatures (from 250 to 360 °C at atmospheric pressure) at which undesired by-products and coke (carbonaceous deposits) reduce the selectivity to DME and lead to catalyst deactivation.⁴ Thus, to produce DME as efficiently as possible, it is of great interest to search for catalysts reaching high methanol conversions at lower temperatures (<250 °C).

Materials which are highly promising in meeting such requirements are heteropolyacids (HPAs). Existing in a large diversity of structures, these metal–oxygen clusters possess a very high Brønsted acidity, approaching the super-acid...
region. Therefore, they generally allow efficient operation under milder conditions than conventional acid catalysts.5 The most studied HPAs, which stand also at the heart of our work, are those having the Keggin structure.6 In a Keggin unit, the acidic protons stabilize an heteropolyanion having the formula [XM12O40]n−, X being the heteroatom (often P5+, Si4+) and M being the addenda atom (transition metal, typically Mo6+, W6+).3,6 More precisely, the heteropolyanion is made of a central XO4 tetrahedron, surrounded by 12 MO6 octahedra. It contains 3 types of oxygen atoms: central (Oa), bridging, and terminal (Ot) ones. The bridging ones are either corner-sharing (O3) or edge-sharing (O5).7 In the hydrated solid, Keggin units are coordinated with crystallisation water molecules. Most commonly, six crystallisation water molecules are contained per Keggin unit, forming a body-centered cubic structure with Keggin anions at the lattice points and acidic H2O+ bridges along the faces.8 With the aim of getting high methanol conversions at low temperatures, the most studied Keggin HPAs for the methanol-to-DME process are the most acidic ones, namely H3PW12O40 and H4SiW12O40.5

In the present paper, we provide a deeper understanding of the catalytic potential of the H3PW12O40 and H4SiW12O40 solids in the gas phase dehydration of methanol to DME. As all HPAs, these solids exhibit a so-called “pseudo-liquid” behavior. This means that polar molecules such as alcohols and ethers may be absorbed into the solid’s bulk.2,9–11 As a direct consequence, catalytic reactions involving these polar molecules potentially take place both within the bulk and at the surface of the solid. In the case of methanol however, opinions differ in the literature when it comes to qualify its dehydration to DME over solid HPAs as bulk-type or surface-type. For instance, Shikata et al.12 state that H3PW12O40 behaves as a pseudo-liquid under methanol, the latter reacting in the solid bulk. In contrast, Alharbi et al.13 state that the same H3PW12O40 operates only through surface-type catalysis in the methanol-to-DME process. In both cases, the authors are categorical; but none of them does consider the potential impact of the experimental conditions. To clarify this point of disagreement is precisely the aim of our work; to use the operando methodology is our strategy. The term operando means “working/operating” in Latin; and operando characterization is defined as a “combined spectroscopic measurement and simultaneous online measurement of catalytic activity/selectivity values during catalytic reaction studies”14. So, structural changes of the catalyst are monitored in real time, at the moment the reaction takes place, instead of before and after the reaction as it is classically done. Raman was chosen here as the spectroscopic technique as it allows characterizing a catalyst’s bulk without any significant interference from the gas phase.14 By operando Raman monitoring the working HPAs throughout a series of well-chosen experiments, we actually demonstrate that, at one given reaction temperature, a working HPA’s bulk may be 1) accessible or not and 2) active or not, depending on the way the HPA has been brought to the reaction temperature and has been exposed to methanol.

In other words, our work provides the experimental conditions in which the HPAs really behave or not as pseudo-liquids under methanol. Knowing those conditions is crucial not only when using the bulk HPAs themselves as the catalysts, but also when using them as the references to which supported HPA catalysts are compared in terms of catalytic performance. Indeed, truly assessing the interest of supported HPAs is possible only if precisely understanding the behavior of the solid reference. If using the solid reference in conditions which actually not allow its bulk to be active, the supported catalysts might appear more interesting than they really are. Moreover, supported HPA catalysts may also contain HPA crystals, depending on the nature of the support and on the HPA loading. It has even been shown that, in the case of H3PW12O40 and H4SiW12O40 supported on TiO2, the conversion of methanol per gram of HPA is actually better with an amount of Keggin units corresponding to 2.3 monolayers (thus exposing HPA crystals) than with an amount corresponding to 1 single monolayer (thus without, or less, crystals).4 According to the authors, this is related to the fact that, when interacting directly with the support’s surface, the HPA’s acidic protons are less available for the catalytic reaction. In other words, supported HPA catalysts may work even better in the methanol-to-DME process when containing HPA crystals on the surface of which the Keggin units are not directly in contact with the support. However, without precisely understanding in which conditions the bulk of such HPA crystals also contributes to convert methanol, one can actually not guaranty to fully exploit the catalytic potential of his supported HPA catalysts.

2. Experimental section

2.1. Chemicals and catalysts

H3PW12O40 (hereafter HPW12) and H4SiW12O40 (hereafter HSiW12) have been purchased from Sigma-Aldrich in the form of H3PW12O40·xH2O and H4SiW12O40·xH2O (reagent grade). The powders have 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 6 for both HPW12 and HSiW12 (the thermogravimetric profiles are supplied in the ESI† on Fig. S1 and S2). For operando Raman monitoring, the HPW12·6H2O and HSiW12·6H2O powders have 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. Operando Raman tests

Operando catalytic tests have been performed under atmospheric pressure in a set-up combining Raman spectroscopy with online product analysis. The set-up was inspired by the one of B. Weckhuysen.15,16 The powdered samples (100 mg) have been introduced into a quartz reactor with optical windows which allowed characterizing the working HPAs.
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. A black box covered the whole setup to avoid disturbances from sunlight.

In all experiments, Raman spectra have been measured continuously with time-on-stream, from the start of the pre-treatment (if present) to the end of the reaction. In-between two successive spectra, irradiation was always shut off. Indeed, a previous work of us has shown that a flow of methanol renders an HPA sensitive to laser-induced heating if the system is irradiated without interruption.\textsuperscript{17} A Kaiser RXN spectrometer was used (diode-pumped frequency doubled Nd-YAG 1 laser with 532 nm wavelength, power ca. 14 mW measured at the moment of the experiments instead of the nominal 50 mW due to aging, Mk II filtered probe head with 5.5 inch noncontact objective, spot-size ca. 100 μm). The resolution was 3 cm\textsuperscript{-1}. The spectrometer had an objective by which the laser beam was focused at a distance of about 14 cm. The acquisition consisted of 15 accumulations (1 second of exposure) for each spectrum.

The reaction has always been performed under a flow of nitrogen saturated with 10 vol% of methanol (the saturator containing the liquid methanol was set at 15 °C and at atmospheric pressure). 150 °C has been chosen as the reaction temperature. Indeed, as the interest of using HPAs is the possibility of operating them under mild conditions, temperatures around 150 °C are generally used in the literature dealing with methanol dehydration over HPAs.\textsuperscript{4,12,13} The total inlet gas flow (either pure nitrogen during a pre-treatment, or methanol-saturated nitrogen during a reaction phase) was always of 100 mL min\textsuperscript{-1}. In order to evaluate the catalytic performance, the outlet gas flow has been analyzed every 5.5 minutes by an Interscience compact gas chromatograph equipped with a Rtx-1 1.5 μm column (15 m × 0.32 mm) followed by a flame ionization detector, a Poraplot Q (2 m × 0.32 mm) and a Molsieve 5 Å column (5 m × 0.32 mm) followed by a thermal conductivity detector, and two Poraplot Q columns (2 m and 8 m × 0.32 mm) followed by a second thermal conductivity detector. The catalytic performance has been evaluated by calculating the conversion of methanol ($C_{\text{MeOH}}$/%) and the selectivity to DME ($S_{\text{DME}}$/%) as follows:

$$C_{\text{MeOH}} = \left( \frac{A_{\text{MeOH}}^{\text{in}} - A_{\text{MeOH}}^{\text{out}}}{A_{\text{MeOH}}^{\text{in}}} \right) \times 100$$

$$S_{\text{DME}} = \left( \frac{A_{\text{DME}}^{\text{out}}}{A_{\text{MeOH}}^{\text{out}}} \right) \times \frac{A_{\text{M}}^{\text{in}}}{A_{\text{MeOH}}^{\text{in}}} \times k \times 100$$

where $A$ is the chromatographic peak area, $f$ is the calibration factor relating the chromatographic peak area of DME to the latter’s percentage in the gas flow, and $S_{\text{DME}}$ is the initial percentage of methanol in the gas flow (10%), and $k$ is the stoichiometric factor between methanol and DME (2). Actually, DME was always the only product of methanol conversion detected here (calculated $S_{\text{DME}}$ always around 98%). Therefore, only the conversion levels are discussed in section 3. The aim of the work being to find out how to exploit the catalyst bulk in addition to its surface, calculating TOF values is not relevant. Indeed, in the case of a “surface + bulk” reaction, internal diffusion comes into play which makes it senseless to compare the overall TOF value to the one resulting of an exclusively surface-type reaction. The aim here is to increase the number of catalytic sites contributing to the reaction (by activating the bulk sites in addition to the surface ones), whatever their TOF.

In a first series of experiments, the behavior of HPW12 and HSIW12 in the reaction of methanol has been studied at 150 °C without any thermal pre-treatment at higher temperature. The hexahydrated HPAs have simply been heated under nitrogen to the reaction temperature 150 °C (10 °C min\textsuperscript{-1}). Then, once their Raman signal was stable, the reaction has been launched. For simplicity, these samples will be called “non-pre-treated” in the discussion of the results, even if leaving them for a certain time under nitrogen at 150 °C before launching the reaction is also a kind of pre-treatment. In a second series of experiments, the catalytic behavior of the two HPAs has again been studied at 150 °C, but this time after a thermal pre-treatment at higher temperature. The latter’s aim was to completely remove the crystallisation water within the solids, without however starting to lose their acidic protons. Indeed, those protons are the catalytically active species. Based on the thermogravimetric and thermodifferential profiles (see Fig. S1 and S2 in the ESI\textsuperscript{f}), 320 °C and 300 °C have been chosen as the pre-treatment temperatures respectively for HPW12 and for HSIW12. Those profiles are well-known in the literature; they have been interpreted here by referring to ref. 5. So, the basic pre-treatment consisted of heating the catalysts (10 °C min\textsuperscript{-1}) under nitrogen to their respective pre-treatment temperatures for 1 hour. Then, the catalytic behavior has been studied as a function of the way to place the anhydrous HPAs under reaction conditions (e.g. cooling directly from the pre-treatment temperature to 150 °C, cooling first to room temperature and then heating up again to 150 °C, exposing to methanol from the room temperature or only once arrived at 150 °C), always with the idea of assessing the activity of the catalyst bulk.

3. Results and discussion

For clarity, the results obtained with HPW12 and with HSIW12 are considered separately. First, the results obtained with HPW12 are shown and discussed. Then, HSIW12 is compared versus HPW12.

3.1. Monitoring of HPW12

3.1.1. No pre-treatment above reaction temperature. In this first section, HPW12 has been used in the simplest way,
namely without having been submitted to any thermal pre-
treatment above the reaction temperature. After introduction
into the operando reactor, the HPW12-6H$_2$O powder has been
heated under nitrogen flow to reaction temperature 150 °C
(10 °C min$^{-1}$), been left at the latter for a certain time
(discussed below), and then been exposed to methanol to
launch the reaction.

The appropriate moment to launch the reaction had to be
determined carefully. Indeed, before it could be monitored
under methanol, HPW12’s Raman spectrum had first to be
stable under pure nitrogen. Otherwise, it would have been
senseless to search for potential methanol-induced effects.
However, it is well-known in the literature that one of
HPW12’s fingerprint bands progressively shifts to higher
wavenumbers upon heating, due to a release of crystallisation
water. It is the symmetric stretch of terminal W=O$_t$ (hereafter
$v_s(W=O_t)$).	extsuperscript{18} Such a shift indeed occurred here upon
heating HPW12 under nitrogen from 20 °C to 150 °C, as
shown by the spectra on Fig. 1. Next to the bands at 990 and
900 cm$^{-1}$, associated to the asymmetric stretches of respec-
tively terminal W=O$_t$ and corner-sharing W–O$_p$–W,	extsuperscript{4,18,19} the
$v_s(W=O_t)$ band shifted from 1006 cm$^{-1}$ at 20 °C to 1010 cm$^{-1}$
upon reaching 150 °C, through the intermediate positions
plotted on Fig. 2a. This shift occurred together with a drop of
intensity and broadening of the band, as the release of
crystallisation water reduces HPW12’s degree of
crystallinity.\textsuperscript{20}

Thus, at 150 °C, the reaction of methanol could only be
launched once the $v_s(W=O_t)$ band had stopped shifting un-
der nitrogen. In other words, it had to be waited until the
crystallisation water content was equilibrated. As shown on
Fig. 2b, this took actually 30 minutes, with a further shift
from 1010 cm$^{-1}$ to 1020 cm$^{-1}$. Then, the band did not shift
anymore. After this stable position had been confirmed for
about 30 additional minutes, the reaction was launched, to-
gether with the operando spectroscopic measurements.

The fact that, on Fig. 2b, the $v_s(W=O_t)$ band stabilizes at
1020 cm$^{-1}$ and not at a higher wavenumber reflects that
HPW12 still contained crystallisation water. Indeed, in the
opposite case, the $v_s(W=O_t)$ band would have reached its
maximum wavenumber of 1024 cm$^{-1}$ (see the spectrum after
heating to 320 °C on Fig. 6 in section 3.1.2). This agrees with
the literature telling that HPW12 keeps at least 3 water mole-
cules per Keggin unit as long as the temperature stays below
200 °C,\textsuperscript{21} and with the thermogravimetric data (Fig. S1 in the
ESI†). As a part of the solid, this residual crystallisation water
needs to be taken into account when discussing as is made
later in this section about HPW12’s catalytic activity. To di-
rectly monitor the water, the O–H Raman signal from 2800 to
3600 cm$^{-1}$ could have been used. This was however not done
here as this signal was no longer intense enough under reac-
tion conditions. The monitoring of water was thus done indi-
rectly in this work as it will be explained.

As shown on Fig. 3, the exposure of HPW12 to methanol
when the reaction was launched immediately affected its
Raman fingerprint.

The $v_s(W=O_t)$ band rapidly shifted from 1020 cm$^{-1}$ (last
spectrum under nitrogen, namely “0 min” under methanol)
back to lower wavenumbers. After 10 minutes under metha-
nol, it stabilized at 1010 cm$^{-1}$. Such a shift reflects an interac-
tion of methanol with the bulk of HPW12. More precisely, it
demonstrates that, in the present experiment, the bulk of
HPW12 was accessible to methanol which penetrated in-
between the Keggin units and so influenced their vibration.
In other words, it shows that HPW12 behaved here as a
pseudo-liquid. The precise reason of the $v_s(W=O_t)$ shift is re-
lated to the way methanol gets bonded to the Keggin units
and will be discussed later.

Fig. S3 in the ESI† shows the same spectra as Fig. 3 but in the
high wavenumber region from 2500 to 4000 cm$^{-1}$. A peak
at 2987 cm$^{-1}$ attributed to the symmetric methyl stretch\textsuperscript{22}
appears as soon as HPW12 gets exposed to methanol, reflecting
the latter’s adsorption onto the catalyst. This was however
not further exploited here as the spectra do not allow
distinguishing between methanol adsorbed at the surface
and within the bulk of the catalyst.

The fact that methanol has entered the bulk of HPW12
does not necessarily mean that it has also reacted in the

\[\text{Fig. 1 In situ Raman fingerprint of HPW12 upon heating the hexahydrate (HPW12-6H}_2\text{O) under nitrogen from 20 °C to 150 °C (10 °C min}^{-1}\text{).} \]
bulk. The next step now is to analyze if methanol has also interacted with the acidic protons. Fig. 4 shows the conversion of methanol (left axis) and the position of HPW12’s $\nu(W=O)$ Raman band (right axis, wavenumber taken at the maximum) as a function of time at 150 °C. 4 phases are distinguished: (a) the last 20 minutes under pure nitrogen (no measure of conversion), (b) 16 hours of catalytic test under 10 vol% of methanol in nitrogen (spectra in the first 20 minutes are those of Fig. 3), (c) 3 hours of flushing under pure nitrogen (no measure of conversion) and (d) again 1 hour of catalytic test.

Fig. 4  Conversion of methanol (left axis) and position of HPW12’s $\nu(W=O)$ Raman band (right axis, wavenumber taken at the maximum) as a function of time at 150 °C (without having thermally pre-treated HPW12 above 150 °C). 4 phases: (a) last 20 minutes under pure nitrogen (no measure of conversion), (b) 16 hours of catalytic test under 10 vol% of methanol in nitrogen (spectra in the first 20 minutes are those of Fig. 3), (c) 3 hours of flushing under pure nitrogen (no measure of conversion) and (d) again 1 hour of catalytic test.

Fig. 2  Position of HPW12’s $\nu(W=O)$ Raman band (wavenumber taken at the maximum) (a) as a function of temperature upon heating the hexahydrate (HPW12·6H2O) under nitrogen from 20 °C to 150 °C (10 °C min$^{-1}$) and (b) as a function of time (still under nitrogen) once having reached 150 °C. The spectra associated to the points on (a) are those of Fig. 1.

Fig. 3  Operando Raman fingerprint of HPW12 (not having been thermally pre-treated above 150 °C) as a function of time under methanol (10 vol% in nitrogen) at 150 °C. Spectrum “0 min” is the last one measured under pure nitrogen before launching the reaction.
nitrogen (no measure of conversion), (b) 16 hours of catalytic test under a flow of 10 vol% methanol in nitrogen (the spectra measured in the first 20 minutes are those of Fig. 3), (c) 3 hours of flushing under nitrogen (no measure of conversion) and (d) again 1 hour of catalytic test under 10 vol% of methanol in nitrogen.

After HPW12’s ν(W=O) band has shifted from 1020 cm⁻¹ in phase a (pure nitrogen) to 1010 cm⁻¹ at the start of phase b (exposure to methanol), its position remains constant throughout the 16 hours of reaction. This indicates that methanol was permanently present within the catalyst bulk. The conversion varies within a narrow range from 4.7% to 5.5% (mean value over the 16 hours of 5.2%). No deactivation is observed. After the 16 hours of reaction, in phase c (flush under pure nitrogen), the maximum of the ν(W=O) band immediately shifts back to higher wavenumbers. After 50 minutes, it finally stabilizes at 1021 cm⁻¹, thus close to the initial 1020 cm⁻¹ in phase a before reaction. In phase d (re-exposure to methanol), the ν(W=O) band shifts again back to 1010 cm⁻¹ and the same conversion of methanol as in phase b is recovered.

The challenge here is to find out if the bulk has contributed or not to the conversion observed in phases b/d, and by this looking at the ν(W=O) band. Indeed, together with the edge-sharing oxygen atoms (O_e), the terminal oxygen atoms (O_t) of HPW12 are reported to be the ones on which methanol gets chemisorbed as a methoxy. DME precisely results from the latter’s reaction with gas phase methanol. However, in phases b/d, the ν(W=O) band does not directly reflect the formation/reaction or not of CH₃O⁻ groups. The position at 1010 cm⁻¹ could still be characteristic of O_t atoms on which methanol gets simply physisorbed. The band has thus to be exploited indirectly, and this is precisely why phase c has been performed.

In phase c, the reversibility of the methanol-induced ν(W=O) shift to 1010 cm⁻¹ is actually informative. Indeed, to react, methanol has first to modify the secondary structure formed by the Keggin units and the crystallisation water. Precisely, it has to displace the water as otherwise, it cannot get protonated by the acidic protons. This is known in the literature, but the conditions in which it really occurs are not explored. Here, it means that, if methanol had succeeded to react with all the bulk protons in phase b, the nitrogen flush in phase c would have left behind an anhydrous bulk. However, the characteristic ν(W=O) wavenumber of anhydrous HPW12 is 1024 cm⁻¹ (as measured in situ after complete dehydation at 320 °C, not shown here) and not 1021 cm⁻¹ as observed on Fig. 4. So, only two explanations for the observed 1021 cm⁻¹ are possible: either methanol has not displaced the crystallisation water here and was simply physisorbed through hydrogen bonds with HPW12’s O_e atoms (taking the place of missing crystallisation water that had been removed upon heating to 150 °C); or the bulk was really anhydrous in phase c but the nitrogen flush has left behind a rest of non-converted chemisorbed methanol which gave rise to a shift of the ν(W=O) band’s maximum from 1024 to 1021 cm⁻¹. The next section 3.1.2, dealing with anhydrous HPW12, will allow understanding whether the second explanation really makes sense or not. Then, the discussion about Fig. 4 will be resumed and concluded in section 3.1.3.

3.1.2. With pre-treatment above reaction temperature. In this section, HPW12 has been used as a catalyst after having been submitted to a thermal pre-treatment above the reaction temperature. The HPW12·6H₂O powder has been heated under nitrogen to 320 °C (10 °C min⁻¹) for 1 hour. Indeed, as mentioned before, 320 °C is the temperature at which HPW12 loses all its crystallisation water (see the thermogravimetric profile on Fig. S1 in the ESI†). Afterwards, once at reaction temperature 150 °C, the anhydrous HPW12 has been left for 1 hour under nitrogen flow. This was just in order to proceed in the same way as in section 3.1.1; it was not mandatory here as the ν(W=O) band was already stable before reaching 150 °C, precisely since the dehydration was complete at 320 °C. After this hour, the reaction has been launched by feeding the methanol-containing flow.

The first experiment contained two parts. Fig. 5 shows the temperature program (left axis) and the conversion of methanol (right axis) in the first part. Phase a is the pre-treatment under pure nitrogen. Phase b is the reaction phase under 10 vol% of methanol in nitrogen.

In phase b, the conversion of methanol slowly increases with time-on-stream, from 3% in the first hour to 9% after 7 hours. So, the mean conversion over the 7 hours of reaction is 6%, what is close to the 5% observed with the hydrated HPW12 in section 3.1.1 (Fig. 4). Fig. 6 shows, as a function of time, the operando Raman spectra of the anhydrous HPW12 which have been measured simultaneously with the conversion plotted on Fig. 5, in the first 150 minutes of reaction. The spectrum “0 min” is actually the last one measured in phase a under pure nitrogen.

In contrast to what was observed on Fig. 3 and 4 in section 3.1.1, the exposure of HPW12 to methanol does not induce any shift of the ν(W=O) band here on Fig. 6. The latter remains at 1024 cm⁻¹, namely the characteristic wavenumber of anhydrous HPW12. So, either methanol did not enter the anhydrous bulk; or it did enter but its interaction with the anhydrous Keggin units was not detectable. In the latter case, it would mean either that methanol interacted here with another oxygen atom than O_e; or that it still interacted with O_e but without affecting the observed ν(W=O) wavenumber. Monitoring the evolution of the ν(W=O) band upon nitrogen-flushing as done in section 3.1.1 (Fig. 4) after the exposure to methanol was not bringing any new information here, as no change has been observed with the band remaining at 1024 cm⁻¹ (not shown). Three more steps have thus been performed to understand the system. They constitute the “second part” of the experiment. Fig. 7 focuses on this second part. It shows the temperature program applied (left axis) and, if appropriate, the conversion of methanol (right axis) during the different phases. Phase a is actually the end of the reaction phase b of Fig. 5; the flow contained still 10 vol% of methanol. Phase b is a flushing phase under
pure nitrogen. Phase c is a second reaction phase under 10 vol% of methanol in nitrogen. The precise progress of each phase is described/discussed hereafter. Every time there is a circle marked on the temperature program, the corresponding Raman spectrum is shown on Fig. 8.

First, in order to stop the reaction phase of the first part of the experiment (the phase b of Fig. 5, of which the last 20 minutes actually correspond to the first 20 minutes of phase a on Fig. 7), the HPW12–methanol system has been cooled down from 150 °C to room temperature (phase a on Fig. 7, from 20 minutes). The last spectrum measured at 150 °C is the “1” on Fig. 8; it has its $\nu_4(W=O_4)$ band at 1024 cm$^{-1}$ (exactly as the spectra of Fig. 6 measured from 4.5 to 7 hours earlier). At 100 °C, the conversion of methanol dropped to zero (Fig. 7), still without the $\nu_4(W=O_4)$ band being shifted from 1024 cm$^{-1}$ (spectrum 2 on Fig. 8). Nevertheless, the story is not over. Once the temperature was down to 25 °C, a spectral change has finally been observed: the $\nu_4(W=O_4)$ band shifted from 1024 to 1010 cm$^{-1}$ (spectrum 3 on Fig. 8). However, there is no other way to explain this shift of the maximum of the $\nu_4(W=O_4)$ band away from its initial 1024 cm$^{-1}$ – the characteristic value for anhydrous HPW12 – than by evoking methanol entering the bulk. So, at 25 °C, methanol was flowing through the bulk. Then, as shown in phase b on Fig. 7, the system has been nitrogen-flushed for a while at 25 °C. After, it has been heated up again. Upon reaching 150 °C, instead of having shifted back to 1024 cm$^{-1}$, the $\nu_4(W=O_4)$ band was still positioned at 1011 cm$^{-1}$ (spectrum 4 on Fig. 8). Even after 1 hour under nitrogen flow, it did not move further (spectrum not shown). This means that there was a chemisorbed rest of methanol within the bulk of HPW12 that did not desorb upon nitrogen-flushing. Indeed, the only other process that could have induced an irreversible change of the $\nu_4(W=O_4)$ band would have been the modification of the Keggin structure itself, for example through the extraction of some of its oxygen atoms. However, this is reported to be unlikely to happen under methanol at such a low temperature. Then, in this state, HPW12 has been
exposed to methanol once again (phase c on Fig. 7). Spectrum 5 on Fig. 8 is representative of the whole reaction phase. It has its $\nu_s(W=O)$ band at 1010 cm$^{-1}$, exactly as at 25 °C. So, in that second reaction phase, methanol was flowing through the bulk, exactly as at 25 °C. The non-shift of the $\nu_s(W=O)$ band from 1024 cm$^{-1}$ in the first part of the experiment, on Fig. 6, became then clear: it was not due to the non-detectability of the interaction of the anhydrous HPW12 with methanol; it was due to the fact that methanol was not even penetrating the anhydrous bulk. As shown on Fig. 7, the result of the penetration of methanol into the bulk was a conversion of nearly 40%, what is four times the conversion observed in the first reaction phase on Fig. 5/in the first 20 minutes on Fig. 7. This drastic increase can only mean that methanol was not only penetrating but also reacting in the bulk. So, over the same anhydrous HPW12, in one and the same experiment, at one and the same reaction temperature, the methanol-to-DME process has turned from surface-type (Fig. 5 and 6) to bulk-type (Fig. 7 and 8). After the reaction phase of Fig. 7, a nitrogen-flush has actually been performed for 3 hours, still at 150 °C. This did however not affect the position of the $\nu_s(W=O)$ band, which remained at 1010 cm$^{-1}$ (not shown). Thus, exactly as during the flush in phase b after the exposure to methanol at 25 °C, the flow of methanol left traces in the bulk which prevented the $\nu_s(W=O)$ band from shifting back to higher wavenumbers. This will be of importance later in section 3.1.3.

In a second experiment, HPW12 has again been dehydrated under nitrogen for 1 hour at 320 °C. However, this time, the anhydrous HPW12 has first been cooled from
320 °C down to 25 °C, before being heated up again to reaction temperature 150 °C. Fig. 9 shows the temperature program (left axis), and the conversion of methanol (right axis). Phase a is the pre-treatment phase. As indicated, the “cooling to 25 °C-heating back to 150 °C” part is actually the equivalent of the phases a and b of Fig. 7 both together; except that here, there is no exposure to methanol at 25 °C. Indeed, the whole phase a has been performed under pure nitrogen. Phase b is the reaction phase under 10 vol% of methanol in nitrogen.

In phase b, the conversion of methanol does not exceed 10%. It is actually of the same order as the conversion observed on Fig. 5, in the first part of the previous experiment. On the operando Raman spectra measured simultaneously (not shown), HPW12’s ν3(W=O) band does not shift with time-on-stream from its initial position at 1024 cm⁻¹ (end of phase a). Again, this corresponds to what was observed in the first part of the previous experiment (Fig. 6). So, in this second experiment, the anhydrous bulk of HPW12 was again inaccessible. However, exactly as in the second part of the previous experiment (Fig. 7), there was a cooling step to 25 °C before reaction. This means that, in the previous experiment, it was not the cooling step alone which enabled the reaction to take place within the anhydrous bulk (afterwards at 150 °C). It was the cooling step combined with the exposure to methanol. The low temperature – 25 °C – has indeed rendered the anhydrous bulk accessible. However, if the latter had not been exposed to methanol still at 25 °C, it would have lost its accessibility again during the heating step back to 150 °C (as it is the case here on Fig. 9). In other words, it was the penetration of methanol into the bulk at 25 °C which allowed maintaining the latter accessible up to 150 °C. Indeed, as reflected by the ν3(W=O) band on spectrum 4 of Fig. 8, there was methanol in the bulk which survived the nitrogen flush (phase b of Fig. 7) performed right after the exposure at 25 °C (phase a of Fig. 7). This residual methanol residing in-between the Keggin units was sufficient to maintain the bulk’s accessibility during the heating step back to 150 °C.

In summary, the experiments performed in this section demonstrate that the bulk of anhydrous HPW12 can contribute to the conversion of methanol, provided that it gets exposed to methanol at 25 °C before being heated to the reaction temperature. Otherwise, it is inaccessible at that reaction temperature and the reaction occurs exclusively at the surface. To our knowledge, this has never been reported before. Indeed, cooling a catalyst directly from the pretreatment temperature to the reaction temperature is the obvious way to proceed. However, by doing so with HPW12, three-fourths of the conversion that could actually be reached are lost. So, enabling the bulk to participate to the reaction, through the way found here thanks to operando monitoring, is really worthy to be done.

3.1.3. Role of crystallisation water and meaning of the ν3(W=O) wavenumber under reaction conditions. In contrast to the anhydrous HPW12 used in section 3.1.2, the hydrated HPW12 used in section 3.1.1 (which had not been submitted to a thermal pre-treatment at 320 °C) did not need any additional step to be able to absorb methanol into its bulk at 150 °C (Fig. 3 and 4). However, the fact that methanol so easily penetrated the hydrated bulk does not directly mean that it also came to react in it. Indeed, on hydrated Keggin units, methanol needs first to displace the residual crystallisation water.²,⁷ If it does not, it can still get physisorbed but it cannot get chemisorbed. Thus, it cannot react.

In light of the results of section 3.1.2, the bulk of the non-pre-treated HPW12 of section 3.1.1 was actually rather inactive. Indeed, as mentioned in relation to Fig. 7, methanol leaves residues when it gets nitrogen-flushed from the anhydrous bulk after reaction, residues which prevent the ν3(W=O) band from shifting back from 1010 cm⁻¹ to higher

![Fig. 9](image-url) Fig. 9 Second experiment including a thermal pre-treatment of HPW12 above the reaction temperature 150 °C – temperature program (left axis) and conversion of methanol (right axis) as a function of time during (a) the thermal pre-treatment under pure nitrogen and (b) the reaction under 10 vol% of methanol in nitrogen.
wavenumbers. However, when the non-pre-treated HPW12 was nitrogen-flushed (phase c on Fig. 4), its $\nu_{v}(W=O)$ band shifted back to 1020 cm$^{-1}$, so to the same position as before reaction (phase a on Fig. 4). Thus, on most of the bulk Keggin units, the crystallisation water cannot have been displaced by methanol. In other words, most of the bulk Keggin units cannot have been active. Actually, methanol can only have physisorbed (hydrogen-bonded) in the bulk where it was possible (namely where some crystallisation water had been released upon heating to 150 °C), so inducing the shift from 1020 to 1010 cm$^{-1}$ observed on Fig. 3 and 4 (phase b). As a reminder, on Fig. 1 and 2, the opposite shift from 1006 cm$^{-1}$ (initial position of the hexahydrate at 20 °C) to 1020 cm$^{-1}$ (equilibrium at 150 °C) was precisely due to the loss of hydrogen bonds induced by the partial release of crystallisation water upon heating. Observing a shift from 1020 cm$^{-1}$ back to lower wavenumbers when recovering hydrogen bonds in flowing methanol makes thus sense. Upon nitrogen-flushing, the physisorbed methanol is then released again and the $\nu_{v}(W=O)$ band shifts again back to 1020 cm$^{-1}$.

How significantly the activity of the bulk is decreased due to the crystallisation water appears as comparing the conversions on Fig. 4 (non-pre-treated HPW12 – 5% after 7 hours), 5 (anhydrous HPW12 of which the bulk was inaccessible – 9% after 7 hours) and 7 (anhydrous HPW12 of which the bulk was accessible thanks to the pre-exposure to methanol at 25 °C – 35% after 7 hours). Indeed, as discussed in section 3.1.2, the 9% of conversion on Fig. 5 can be fully assigned to the surface of the anhydrous HPW12. In other words, 9% is the maximum conversion that the anhydrous surface could reach here. So, on Fig. 7, at least 26 of the 35% of overall conversion (bulk + surface) can be assigned to the bulk of the anhydrous HPW12. Thus, with an overall conversion of 5% (bulk + surface) on Fig. 4, the bulk of the non-pre-treated HPW12 was at least 5 times less active than the bulk of the anhydrous HPW12 (reaction conditions having been the same). To our knowledge, up to here, such a comparison of hydrated and anhydrous HPW12 had never been done. However, the results of it should absolutely be taken into account when choosing between pre-treating or not an HPW12 sample to be used in the methanol-to-DME reaction.

To summarize the two preceding paragraphs, crystallisation water appears to have a double role within the bulk of non-pre-treated HPW12. First, it maintains the bulk accessible to methanol. Indeed, if removing water and trying to launch the reaction directly at 150 °C without having pre-exposed the sample to methanol at 25 °C, the bulk is inaccessible. This is a priori a positive point. However, the second role is a negative one. Indeed, crystallisation water also prevents methanol from reaching the catalytically active protons. So, at the end, the non-pre-treated/hydrated bulk is rather inactive compared to the anhydrous one which has been pre-exposed to methanol at 25 °C. “Rather” inactive means that there may always be some Keggin units which have lost more crystallisation water than the others, and are thus active. Indeed, it has to be remembered that it is the maximum of the $\nu_{v}(W=O)$ band which has been monitored here. The position of this maximum indeed reflects the behavior of most of the bulk Keggin units, but it does not exclude that some of them behave differently. In this sense, it is still not clear whether the 5% conversion observed with the non-pre-treated/hydrated HPW12 on Fig. 4 came exclusively from the surface or if there was also a contribution from the bulk. So, in the case of the non-pre-treated/hydrated HPW12, it can be stated neither that the reaction is purely “surface-type” nor that the reaction is purely “bulk-type”. It can only be stated that the bulk is in a “low activity state”. Actually, this is exactly the point that explains the discrepancy between the works of Shikata et al.$^{12}$ and Alharbi et al.$^{13}$ mentioned in the Introduction. Without having paid attention to it, both groups have worked with hydrated HPW12. Indeed, they both report to have pre-treated their samples at reaction temperature (120–150 °C) for 1 h in nitrogen flow, thus exactly as it was done here in section 3.1.1. However, they came to contradictory conclusions about the surface-type or bulk-type character of the reaction, because they both neglected – without being aware of it – a different aspect of the role of the residual crystallisation water. Alharbi et al. state that the reaction is surface-type based on the fact that their catalytic results do not reflect significant internal diffusion limitations. On one hand, this makes sense. Indeed, the crystallisation water is likely less stable at the surface than in the bulk. Thus, knowing that one effect of crystallisation water is to prevent methanol from reaching the acidic protons, the surface protons are actually more likely to be the active ones. Nevertheless, even if the surface was really the main catalytic actor, the results shown in the present work strongly suggest that methanol was also contacting the bulk of the authors’ samples. Indeed, this is the first role of crystallisation water discussed here: maintaining the bulk accessible to methanol. However, as explained above, one cannot qualify the reaction as purely “surface-type” as long as there is a penetration of methanol into the bulk. Conversely, Shikata et al. state that the reaction is bulk-type because they observed that methanol was penetrating into the bulk during absorption–desorption measurements at reaction temperature. Indeed, this agrees with the present work. However, the authors should have considered that residual crystallisation water prevents methanol from reaching the acidic protons (second role discussed here), so limiting the catalytic potential of the bulk. Exactly as Alharbi et al., they could thus have nuanced their statement by not necessarily assigning all their observed conversion to the activity of the bulk. So, on one hand, Alharbi et al. completely reject a possible contribution of the bulk (while methanol actually penetrates the latter thanks to the residual crystallisation water), whereas Shikata et al. assign all their conversion-related observations to the bulk (while the latter’s activity is actually limited due to the presence of residual crystallisation water). Both statements are actually relevant in light of the type of experiments performed by the respective authors, but they should have been nuanced. By doing so,
they are no longer contradictory. However, in any case, the present work shows that HPW12 should not be used in a dehydrated state for the methanol-to-DME reaction. It should be dehydrated and then be exposed to methanol at 25 °C before being heated to reaction temperature. In this way, there is no doubt about what happens: the bulk is the main catalytic actor, and this should absolutely be exploited as it leads to a much higher conversion.

3.1.4. Comment about the shift of the να(W=O) band under methanol at 25 °C. One could have been tempted to justify the shift of the να(W=O) band from 1024 to 1010 cm⁻¹ at 25 °C on Fig. 8 through a rehydration of the Keggin units with water molecules having accumulated at the surface of HPW12 during the first part of the first experiment (temperature program and conversion of Fig. 5), and finally penetrating into the bulk upon cooling down to 25 °C in the second part of the experiment. This is senseless for the following reasons. First, if this had been the case, the methanol conversion obtained after heating from 25 °C back to 150 °C (thus during phase c of Fig. 7) would have been as low as on Fig. 4 in section 3.1.1 “No pre-treatment above reaction temperature”. Indeed, a rehydration would have led HPW12 back to its initial state before the thermal pre-treatment at 320 °C. Secondly, in another experiment (not shown), the second part of the first experiment (temperature program and conversion of Fig. 7) has been performed independently of the first part. So, HPW12 has been dehydrated under nitrogen at 320 °C, then it has been directly cooled down to 25 °C (without any stop at 150 °C to check the performance) and exposed to methanol at 25 °C, and finally it has been heated up again to reaction temperature 150 °C. By doing so, there can thus not have been any water in the system during the step at 25 °C.

Nevertheless, the να(W=O) band shifted exactly as on Fig. 8 at 25 °C, and the resulting conversion at 150 °C was also exactly the same as on Fig. 7. This confirms that the να(W=O) band shifts due to the flow of methanol, independently of the presence of water resulting from the conversion of methanol (which does not occur at 25 °C). Moreover, the fact that the να(W=O) band remains at 1010 cm⁻¹ on Fig. 8 upon launching the reaction at 150 °C may not either be justified through a rehydration of the Keggin units with water molecules resulting from the ongoing dehydration of methanol at the surface of HPW12, without the involvement of the bulk reaction. Indeed, if this had been the case, the same shift to 1010 cm⁻¹ would have been observed on Fig. 6 in the first part of the first experiment (temperature program and conversion of Fig. 5). However, it is not observed; the να(W=O) band stays at 1024 cm⁻¹ throughout the reaction. Actually, the bulk of HPW12 cannot have been rehydrated – neither with water molecules produced at the surface nor with ones produced in the bulk – during the reaction at 150 °C of Fig. 7 and 8; otherwise, the conversion would have dropped back to the 5% observed on Fig. 4 in section 3.1.1 “No pre-treatment above reaction temperature”. The water produced during the reaction thus leaves HPW12, exactly as the excess methanol having not been converted.

3.2. Performance of HSiW12 versus HPW12

The first part of this work has allowed finding out how to properly exploit the bulk of HPW12 in the methanol-to-DME reaction. In the second part, exactly the same experiments have been repeated with HSiW12, another Keggin HPA. Exactly as observed with HPW12, the absence of a thermal pre-treatment had a negative impact on the conversion of methanol as it implied the presence of residual crystallisation water (not shown here). The latter appeared to play exactly the same role as in the case of HPW12. It was the anhydrous HSiW12 sample (obtained after having pre-treated the initial HSiW12·6H₂O powder for 1 hour at 300 °C) which allowed reaching the highest conversion. Actually, it showed exactly the same behavior in terms of bulk accessibility as the anhydrous HPW12. Namely, to have an active bulk at 150 °C, it needed to get pre-exposed to methanol at 25 °C. Otherwise, methanol did not even penetrate the bulk at 150 °C. This appears on Fig. 10, which is the equivalent of Fig. 7 in section 3.1.2; and on Fig. 11, which shows selected operando Raman spectra corresponding to the situations marked by circles on Fig. 10. On Fig. 10, the temperature program (left axis) and the conversion of methanol (right axis) are shown as a function of time as the anhydrous HSiW12 is (a) cooled from 150 °C down to 25 °C after a first reaction phase, still under 10 vol% of methanol in nitrogen; (b) nitrogen-flushed at 25 °C and then heated again, still under pure nitrogen, to 150 °C; and (c) submitted to a second reaction phase at 150 °C under 10 vol% of methanol in nitrogen.

In the second reaction phase (phase c on Fig. 10), the conversion was about 4 times higher than in the first one (phase a on Fig. 10, in the first 20 minutes before cooling down). Indeed, on spectrum 1 of Fig. 11, which is representative of the whole first reaction phase, the να(W=O) band is positioned at 1019 cm⁻¹. However, this is exactly the same position as before reaction; namely the characteristic position for anhydrous HSiW12. So, in the first reaction phase, the flow of methanol did not affect the να(W=O) band, what reflects that it did not penetrate the bulk of HSiW12. Then, as the sample was cooled down still in flowing methanol, the να(W=O) band shifted from 1019 cm⁻¹ at 150 °C to 1004 cm⁻¹ at 25 °C (spectrum 2 on Fig. 11). This reflects that, at 25 °C, methanol penetrated into the bulk of HSiW12. Finally, as the system was heated again to 150 °C and the second reaction phase was launched, the να(W=O) band remained at 1004 cm⁻¹ (spectrum 3 on Fig. 11). So, in contrast to the first reaction phase, the second one occurred with methanol reacting in the bulk of HSiW12.

First, these results show that the discussions held in the present work likely apply to Keggin HPAs in general. Second, they show that, in the most active situation (anhydrous and pre-exposed to methanol at 25 °C), the conversion of methanol is lower over HSiW12 than over HPW12 (25% vs. 35% at
the end of the second reaction phases respectively on Fig. 10 and 7). This means that the lower acid strength of HSiW12 is not compensated by its higher number of protons (4 per HSiW12 Keggin anion vs. 3 in HPW12) in the methanol-to-DME reaction. In other words, the acid strength is the predominating factor controlling the performance of a Keggin HPA in methanol dehydration, not the number of protons.

4. Conclusions

The catalytic behavior of HPW12 and HSiW12, two Keggin HPAs, has been monitored by operando Raman spectroscopy in the gas phase dehydration of methanol to DME. The aim was to find out in which conditions the HPAs’ bulk contributes or not to the reaction, and to understand why. As all operando tests have been performed at low temperature, namely 150 °C, the selectivity to DME was always 100%. On one hand, when the initially hexahydrated HPAs were simply heated from room temperature to 150 °C (no thermal pre-treatment), their bulk was accessible to methanol. However, as the HPAs still contained crystallisation water which trapped the acidic protons, the overall catalytic activity (bulk + surface) was low. On the other hand, when the HPAs were thermally pre-treated in order to completely remove their crystallisation water, their bulk became inaccessible and the reaction became purely surface-type. Regarding the conversion, it actually remained as low as before dehydration. In-between these two situations, our results reveal a way to render the HPAs’ bulk active. The key is to have the bulk simultaneously anhydrous and accessible. This is achieved by: not cooling the HPAs from their pre-treatment temperature (320 °C).
°C and 300 °C respectively for HPW12 and HSiW12) directly to 150 °C; instead, cooling them first to 25 °C, exposing them to methanol at 25 °C, and then heating them again to 150 °C. Indeed, at 25 °C, the anhydrous bulk is accessible to methanol; and, once methanol has penetrated the bulk, even if getting nitrogen-flushed, it does then never completely desorb anymore. This actually maintains the bulk accessible when the system gets heated up again to 150 °C. Then, when launching the reaction, the conversion raises up to about four times the level it had before this procedure. In that situation, the bulk thus contributes to the reaction.

The present work shows that, at one given reaction temperature, the bulk-type or surface-type character of the methanol-to-DME process over Keggin HPAs depends 1) on the presence or not of a thermal pre-treatment, and 2) on the way the reaction is launched. However, there is only one way to fully exploit the bulk: using the anhydrous HPAs which have been pre-exposed to methanol at 25 °C. In the non-pre-treated/hydrated HPAs, the residual crystallisation water appears to have a double role. On one hand, it allows methanol entering the bulk. However, on the other hand, it prevents methanol from reacting on the Keggin units. Actually, if taking into account both aspects, the results of Shikata et al. and Alharbi et al., two groups diverging in their conclusions that the reaction over the non-pre-treated/hydrated HPAs is respectively bulk-type and surface-type, are no longer contradictory.

The present work additionally allowed comparing the performance of HPW12 and HSiW12 as they had both their bulk active. It clearly appeared that HPW12 has a higher activity in the methanol-to-DME reaction than HSiW12. The latter’s lower acid strength is thus the predominant factor, not its higher number of protons.

Abbreviations

HPW12 Phosphotungstic acid
HSiW12 Tungstosilicic acid

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References

17 J. Schnee and E. M. Gaigneaux, Raman monitoring of a catalytic system at work: Influence of the reactant on the


