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# Lifetime of the $H_3PW_{12}O_{40}$ heteropolyacid in the methanol-to-DME process: A question of pre-treatment

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ABSTRACT

$H_3PW_{12}O_{40}$ is a Keggin heteropolyacid (HPA) that nowadays attracts more and more attention as catalyst for the gas phase dehydration of methanol to dimethylether. Here, we investigate its performance in the latter reaction at 250–300 °C, namely under coking conditions. Actually, we address the question whether the elsewhere elucidated procedure allowing to activate the bulk of the $H_3PW_{12}O_{40}$ solid is beneficial or not under conditions leading to the rapid coking/deactivation of $H_3PW_{12}O_{40}$'s surface (through which the bulk gets accessed). Unprecedented, our results show that pre-activating the bulk is actually crucial in the latter conditions, as it allows drastically increasing $H_3PW_{12}O_{40}$'s lifetime (up to 5 times at 300 °C). Indeed, once activated, the bulk stays accessible beyond the deactivation of the surface. However, with its 24 times more protons than provided by the surface, and with the conversion over the latter protons being diffusion-limited, it then contains continuously enough fresh protons being able to take over the job of the other bulk protons that are deactivated (in the sense that they are capped within coke molecules) until having all been solicited/deactivated. As a consequence, the catalyst bed gets fully exploited until the last of its available bulk protons has contributed to the reaction, instead of getting only scarcely exploited as it is the case when the reaction is purely surface-type. So, the results of this work bring considerable insight on how to use a Keggin HPA-based catalyst in a more sustainable way. Furthermore, they allow understanding the performance obtained upon submitting a Keggin HPA to a temperature programmed reaction of methanol from 25 to 300 °C. Indeed, throughout such a reaction, the deactivation profile (e.g. drastic conversion drops vs slow ones) is governed by the nature of the protons (surface vs bulk-type) that are getting deactivated.



## 1. Introduction

Heteropolyacids (HPAs) are nowadays widely used in acid catalysis. Indeed, they possess a very strong Brönsted acidity, approaching the super-acid region, and offer a large diversity of structures [1–3]. In particular, Keggin-structure HPAs – the most easily available ones – currently attract more and more attention as catalysts for the gas phase dehydration of methanol to dimethylether (DME) [4,5]. Thanks to its very low climate impact, DME is one of the most promising renewable fuels for the future. It is non-toxic, non-corrosive, biodegradable in air, and it burns with almost no emission of nitrous oxides or particulates [6,7].

Keggin HPAs are ionic solids made of cubic crystals of $[XM_{12}O_{40}]^{n-}$ heteropolyanions stabilized by acidic $H^+$ counter-cations, with X being the heteroatom (often $P^{5+}$, $Si^{4+}$) and M being the addenda atom (transition metal, typically $Mo^{6+}$, $W^{6+}$) [2,8]. Resulting from the condensation of oxoanions, the heteropolyanion is often called "cluster". It is composed of a central $XO_4$ tetrahedron surrounded by twelve $MO_6$ octahedra [2]. Hereafter, the entity formed by an $[XM_{12}O_{40}]^{n-}$ heteropolyanion/cluster with its n acidic protons (so $H_nXM_{12}O_{40}$) is called "Keggin unit".

As all HPAs, Keggin HPAs show a so-called "pseudo-liquid" behavior. This means that HPA crystals are able to absorb polar molecules such as alcohols and ethers into their solid bulk (the term "bulk" always referring in the present work to the inside of HPA crystals, not to the inside of a heteropolyanion/cluster or Keggin unit) [9–12]. As a consequence, reactions involving the latter molecules potentially occur both at the surface and within the bulk of the crystals. However, in the case of the methanol-to-DME process, it has been shown that the contribution of a Keggin HPA's crystal bulk to the reaction depends on the conditions in which the HPA has been pre-treated [13]. Precisely, to activate a Keggin

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HPA's bulk, one has 1) to dehydrate the HPA, namely to evacuate its crystallization water trapping the acidic protons, and 2) to pre-expose the HPA to methanol at 25 °C before bringing it to the reaction temperature, in order to render its bulk accessible. If not considering point 2), the reaction is limited to the only surface of the HPA crystals as methanol is then unable to penetrate the bulk [13].

In the present paper, we demonstrate how crucial it actually is to activate the bulk of an HPA when aiming to operate the latter sustainably in the methanol-to-DME process. Indeed, at moderate reaction temperatures (100–300 °C), coking is reported to be the main cause of HPA deactivation, and it is particularly problematic insofar as HPAs are difficult to regenerate because of their low thermal stability [8]. However, the bulk activation procedure having been elucidated only recently, it has – to our knowledge – not yet been envisaged that the HPA's sensitivity to coking could depend on whether the reaction is performed through the surface-type or through the bulk-type mechanism. Actually, *a priori*, one could be tempted to presuppose that the access to an HPA's bulk would anyway get obstructed by the coke accumulating at the HPA's surface. Showing that this is not the case is precisely the aim of the present work, in which we focus on the reaction of methanol at 250–300 °C over $H_3PW_{12}O_{40}$ (HPW12 hereafter), the most acidic [8] Keggin HPA. Unprecedented, our results demonstrate that HPW12's bulk plays an important role at the stage of deactivation, and, at the same time, they allow understanding how to interpret the general activity profile obtained upon submitting HPW12 to a temperature programmed reaction of methanol from 25 to 300–350 °C.

## 2. Experimental

### 2.1. Materials

The HPW12 catalyst has been purchased from Sigma-Aldrich in the form of $H_3PW_{12}O_{40}{\cdot}xH_2O$ (reagent grade). In order to evacuate physisorbed water, the powder has been placed overnight under vacuum (<5000 Pa) at room temperature. As revealed by a subsequent thermogravimetric analysis (TGA – performed in a Mettler Toledo TGA/SDTA851 at 10 °C/min and in a 100 mL/min stream of air), the number of crystallization water molecules present per Keggin unit (x) was 6 (see Fig. S1 in the Supplementary Information). Methanol, carried by nitrogen (Praxair 5.0) in the catalytic tests, has also been purchased from Sigma-Aldrich (anhydrous, 99.8%).

### 2.2. Specific surface area measurement

The specific surface area of the HPW12 powder (sieved within 100–200 μm for the catalytic tests) has been measured by nitrogen physisorption in order to determine the fraction of Keggin units located at the surface and within the bulk of the particles. The analyses have been performed at −196 °C with a Micromeritics TriStar 3000 instrument. Before measurement, the samples (120 mg) have been outgassed overnight at 150 °C under vacuum (50 m Torr). The specific surface area has been evaluated by the BET method in the range between 0.05 and 0.30 $P/P^{\circ}$.

### 2.3. Catalytic tests – operando characterization

All catalytic tests have been performed by introducing a given amount (detailed later) of catalyst powder (of which physisorbed water has beforehand been evacuated as described in Section 2.1) sieved within 100–200 μm into a tubular reactor (fixed bed) and by placing the latter under an inflow of nitrogen saturated with 10 vol.% of methanol at atmospheric pressure (the flow having passed through a moisture trap before reaching the catalyst). In each test, the outlet gas flow was analyzed every 5.5 min 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.

In a first series of tests, the reaction has been performed following a temperature program from 25 to 350 °C. Precisely, the HPW12-methanol system has been heated successively from 25 to 50–100–150–200–250–300–350 °C, with each temperature plateau having lasted for 2 h and each ramp having been performed with a rate setpoint of 1 °C/min. Applying such a temperature program to reach 250–300 °C, namely the temperature range of interest in this work, respects the bulk activation procedure described in Section 1 as it leads both to the penetration of methanol into the bulk of HPW12 (by starting to expose the latter to methanol at 25 °C) and to the full dehydration of HPW12 (as the latter's crystallization water gets evacuated upon heating from about 120 °C up to 250 °C, see the TGA profile on Fig. S1). In a second series of tests, the reaction has again been performed following a temperature program, but this time the HPW12-methanol system has been heated from 25 °C directly to 250 °C (setpoint 1 °C/min), temperature at which it has then been maintained for a few minutes to several hours before having been further heated to 300 °C for 3 h (setpoint 1 °C/min). In a third series of tests, the reaction has been performed directly at 250 °C and/or at 300 °C, without HPW12 having been exposed to methanol at lower temperatures. So, HPW12 has been heated from 25 to 250/300 °C under pure nitrogen (setpoint 1 °C/min), and then only it has been exposed to methanol in order to launch the reaction (a procedure that does not allow methanol to penetrate into HPW12's bulk, as explained in Section 1).

All tests have been performed with 30 mg of catalyst and a total inflow of 60 mL/min, except one in which 100 mg of catalyst and a total inflow of 100 mL/min have been used. The latter has been performed with the temperature program from 25 to 350 °C described above (it is part of the first series of tests). Its aim was to monitor the evolution of coke as a function of temperature/time-on-stream by *operando* UV–vis and Raman spectroscopy (in diffuse reflectance mode), what is possible only with a sufficient bed height (provided from 100 mg). It has been performed in the same setup – described in details elsewhere [13]–as all the other tests, with the only difference that the spectrometers were in its case switched on. The reason why not all the tests have been performed in these conditions is that, with 100 mg of catalyst (whatever the flow rate), pressure drop issues arise from 300 °C (likely due to the accumulation of coke), in the presence of which the gas chromatographic analyses are no longer reliable (observed concentrations become aleatory). For the same reason, in Section 3, the spectra measured in the unique *operando* test with 100 mg of catalyst are actually correlated to the catalytic performance only up to 250 °C.

### 2.4. Post-test characterization

After reaction, the HPW12 samples have been recovered and analyzed by TGA (in a Mettler Toledo TGA/SDTA851 at 10 °C/min and in a 50 mL/min stream of air) in order to evaluate the weight-percentage of coke deposited, as well as by Fourier transform infrared (FT-IR) spectroscopy (in transmission mode) in order to check the conservation of the Keggin structure. For FT-IR, an IFS55 Equinox spectrometer (Bruker) equipped with a DTGS detector was used. 100 scans per spectrum were recorded between 400 and 4000 $cm^{-1}$ with a resolution of 4 $cm^{-1}$. Pellets were prepared after dilution of the samples in KBr (Janssens Chimica 99%) by a 100 wt factor. As the Keggin structure was always proven to be maintained, only one spectrum being representative of all analyses is shown on Fig. S2 in the Supplementary Information (with the spectrum before reaction being shown as a reference).

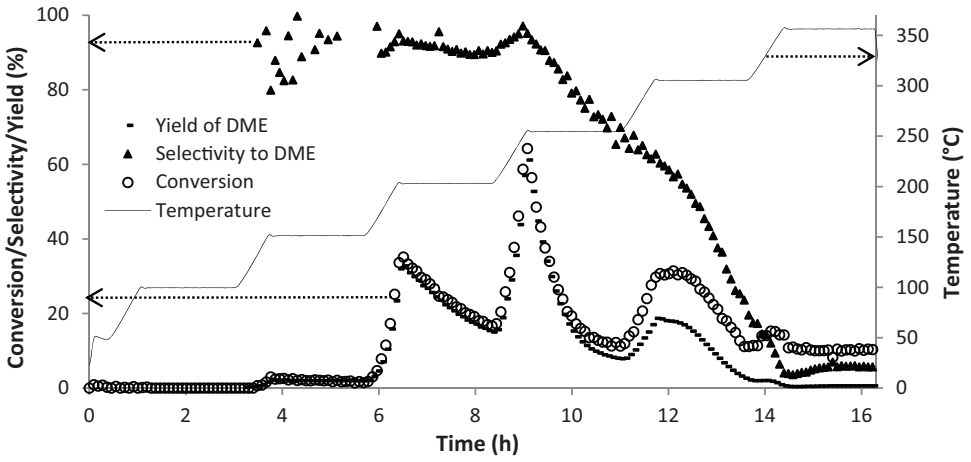


**Fig. 1.** Conversion of methanol, selectivity to DME and yield of DME as a function of time during the temperature programmed reaction of methanol from 25 to 350 °C over HPW12 (30 mg, 10 vol.% of methanol in nitrogen, total inflow of 60 mL/min).

## 3. Results and discussions

### 3.1. Reaction through the bulk activation procedure

#### 3.1.1. Temperature programmed reaction from 25 to 350 °C

Fig. 1 shows the conversion of methanol, the selectivity to DME and the yield of DME obtained as a function of time in the temperature programmed reaction from 25 to 350 °C over 30 mg of HPW12 (60 mL/min).

DME gets produced from 150 °C. Until the start of the plateau at 250 °C, the selectivity to it is always around 90% (the fluctuations at 150 °C being attributed to the high error at very low conversions). Then, until the start of the plateau at 350 °C, it continuously drops (final value of about 4% at 350 °C). Regarding the conversion, 3 kinds of behavior can be distinguished with increasing temperature: 1) at 150, 200 and 250 °C, the conversion continuously drops from the start to the end of the plateau (respectively from 2.5 to 1.5%, from 33 to 14% and from 64 to 11%) – 2) at 300 °C, the conversion is first stable for almost 1 h (at 30%), and only then it drops (to 11% at the end of the plateau) – 3) at 350 °C, the conversion is stable from the start to the end of the plateau (at 10%).

The drops of conversion at 200 and 250 °C cannot have been caused by a rehydration of HPW12 with water resulting from the dehydration of methanol. Indeed, the TGA profile of HPW12 (Fig. S1 in the Supplementary Information) shows that the release of the latter's crystallization water starts at 120 °C and is complete at 250 °C. So, at 250 °C, as well as at 200 °C if no pre-heating has been done at higher temperature, the uptake of water by HPW12 is unfavored. Actually, these drops of conversion are due to coking (indeed the only other HPA deactivation source), as directly reflected by the *operando* UV–vis and Raman spectra measured in the temperature programmed reaction from 25 to 250 °C over a higher catalyst bed (100 mg of HPW12, 100 mL/min of total inflow, reaction stopped at 250 °C for the reason explained in Section 2.3). Indeed, in this second experiment, exactly the same conversion and selectivity profiles as shown on Fig. 1 are obtained (with slightly higher conversions, see Fig. S3 in the Supplementary Information), and the *operando* UV–vis spectra show significant background rises in the visible region (>400 nm) at 200–250 °C (Fig. 2). However, as such background rises are not observed below 400 °C upon heating HPW12 under pure nitrogen (not shown), they can only be due on Fig. 2 to the deposition of carbon, well-known [14] to darken a catalyst bed. For clarity, the UV–vis spectra of Fig. 2 are shown only from 250 to 500 nm (the bands at 250 and 350 nm being due to $O^{2-} \rightarrow W^{6+}$ charge transfer within HPW12) [15]. Notice however that, at 250 °C, the visible background actually rises in a broader wavelength range, namely from 400 to 660 nm (Fig. S4 in the Supplementary Information, showing the same first and last spectra at 250 °C as Fig. 2, but in the full region from 250 to 800 nm). According to [16], this reflects that, at 250 °C, larger coke molecules are formed than at 200 °C. On the *operando* Raman spectra at 200–250 °C (Fig. 3), the deposition of coke is reflected by the bands at 1370 and 1593 $cm^{-1}$ characteristic [17–19] of ring stretches within polyaromatic compounds. The fact that, instead of increasing, the overall intensity of these bands slightly decreases with time-on-stream is attributed 1) to the high sensitivity of Raman intensities to increasing temperature and 2) to the fact that, even if coke is getting more and more abundant, it has such a high visible light extinction coefficient that a 532 nm laser beam can anyway not excite more than the uppermost several tens to one hundred nm [19]. Regarding the Raman bands of HPW12's Keggin structure (at 900, 990 and 1006 $cm^{-1}$), they are visible only on the *operando* spectra below 200 °C (not shown). On Fig. 3, at 200–250 °C, they are absent. Indeed, polyaromatic coke is known to absorb the laser beam so strongly that the signal of the underlying catalyst generally disappears [17,19].

Regarding the conversion profile observed at 300 °C on Fig. 1 (for which there are no *operando* spectra available from the experiment of Figs. 2 and 3), it can be confidently assumed that the drop in the second hour is also due to coking, exactly as the preceding drops at 200 and 250 °C. Indeed, exactly as at 200–250 °C, the only other possible source of deactivation, which is the potential rehydration of HPW12 with water resulting from the dehydration of methanol, can be excluded based on HPW12's TGA profile. However, the question remains why the conversion at 300 °C stays stable in the first hour instead of immediately dropping as observed at 200 and 250 °C, especially as the yield of coke (Fig. S5b in the Supplementary Information, indirectly evaluated by multiplying the conversion by the lack of selectivity remaining after addition of the selectivities on Fig. S5a to DME and byproducts) is permanently higher at 300 °C than at 200 and 250 °C (respectively 6 and 3 times higher). The answer to this question will arise through the next sections.

#### 3.1.2. Reaction at 250–300 °C after heating from 25 °C under methanol

Fig. 4 shows the conversion of methanol, the selectivity to DME and the yield of DME as a function of time in four different experiments performed over 30 mg of HPW12 (60 mL/min) following variants of the temperature program used in Section 3.1.1.

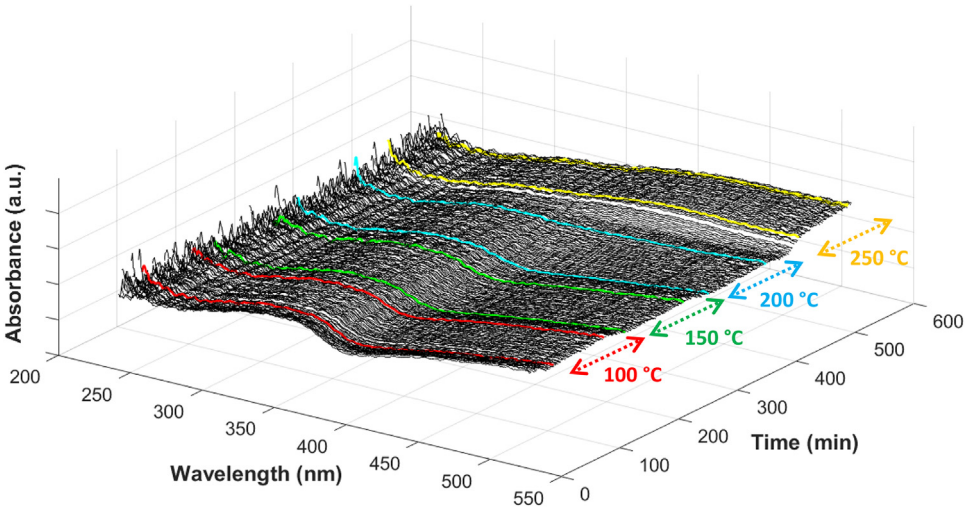


**Fig. 2.** Operando UV–vis spectra of HPW12 as a function of time/temperature in the temperature programmed reaction of methanol over 100 mg of HPW12 and under a total inflow of 100 mL/min. The first and last spectra at each temperature plateau are colored for clarity of the evolution with time-on-stream.

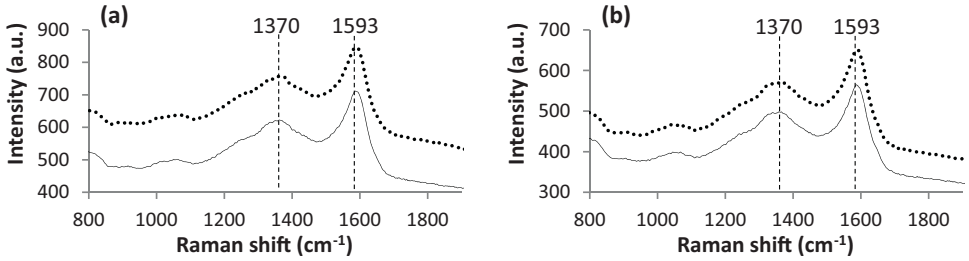


**Fig. 3.** First (dotted line) and last (full line) operando Raman spectra at (a) 200 °C and (b) 250 °C in the temperature programmed reaction of methanol over 100 mg of HPW12 (100 mL/min of total inflow, 10 vol.% of methanol in nitrogen).

In the first experiment (Fig. 4a), HPW12 gets heated under methanol (10 vol.% in nitrogen, exactly as in Section 3.1.1) from 25 °C directly to 250 °C for 7.5 h. The conversion rises during the heating from 25 to 250 °C. Then, once at 250 °C, it immediately drops, exactly as observed on Fig. 1. However, in contrast to what could have been expected from Fig. 1, after 2.5 h, the conversion actually stabilizes around 9% instead of further dropping towards 0. It remains then constant for entire 5 h, before finally slowly decreasing again (see Fig. S6 in the Supplementary Information for the precise evolution after the first 7.5 h at 250 °C). Regarding the selectivity to DME, it drops from 92 to 65% in the first 2.5 h at 250 °C. Then, it continues to drop, but slower (further losing only 11% within the following 5 h). After 7.5 h at 250 °C, its dropping slightly accelerates again (see Fig. S6). So, once the first 2.5 h of deactivation are over, a residual 5% yield of DME is maintained for 5 h before definitely decreasing towards 0.

In the second experiment (Fig. 4b), HPW12 gets heated under methanol from 25 °C directly to 300 °C for 2.5 h (not for longer as, from that time, the further accumulation of coke induces pressure drop issues within the setup). During the heating from 25 °C, the conversion rises until 250 °C is reached. Then, until 300 °C is reached, it drops. Finally, throughout the 2.5 h at 300 °C, it remains stable around 30%. The latter value is the same as observed in the first hour at 300 °C on Fig. 1. So, regardless of whether HPW12 has already worked/been coked for 2 h at 200 °C followed by 2 h at 250 °C (case of Fig. 1), or only during the heating from 25 °C (case of Fig. 4b), the conversion upon reaching 300 °C is the same. What is different however from one case to the other, is the stability of this conversion. Indeed, on Fig. 1, the conversion is stable for only 1 h, whereas here on Fig. 4b, it is stable for 2.5 h. Regarding the selectivity to DME on Fig. 4b, it drops at the end of the temperature rise from 25 °C, namely from 88% at 250 °C to 50% upon reaching 300 °C. Then, once arrived at 300 °C, it remains stable for 1 h, before slowly decreasing towards a final value of 40% at the end of the test. So, within the 2.5 h at 300 °C, the yield of DME loses only 4% (from 15% at the start to 11% at the end), whereas during the 30 min of temperature rise from 250 to 300 °C, it has lost as much as 53% (from 68% at 250 °C to 15% upon reaching 300 °C).

In the third (Fig. 4c) and fourth (Fig. 4d) experiments, HPW12 gets heated from 25 °C directly to 250 °C, then it is left at 250 °C respectively for 30 min and for 3.5 h, and finally it gets further heated to 300 °C respectively for 2.5 and 2 h. In both experiments, the conversion rises during the heating from 25 to 250 °C, exactly as in the 2 previous experiments (Fig. 4a/b). Then, on Fig. 4c, it drops throughout the 30 min at 250 °C, as well as during the successive heating to 300 °C, but only until 280 °C is reached. From then, it remains stable around 26% for 82 min (thus for the 12 min of heating left from 280 to 300 °C, and then for the first hour at 300 °C), before continuously decreasing towards a final value of 15% at the end of the test. On the other hand, on Fig. 4d, the conversion drops in the first 2.5 h at 250 °C, then it stabilizes around 9% (as on Fig. 4a) for 1 h, and finally it rises up again upon heating to 300 °C. Once at 300 °C, it remains stable around 27% for about 35 min, before continuously decreasing towards a final value of 13% at the end of the test. Regarding the selectivity to DME, it shows the same general behavior in both experiments. On Fig. 4c, it continuously decreases from 90 to 85% within the 30 min at 250 °C. Then, it further decreases during the heating to 300 °C, reaching 68% at 280 °C. From then, it decreases slower, until reaching 44% at the end of the test. On Fig. 4d, it continuously decreases within the 3.5 h at 250 °C,

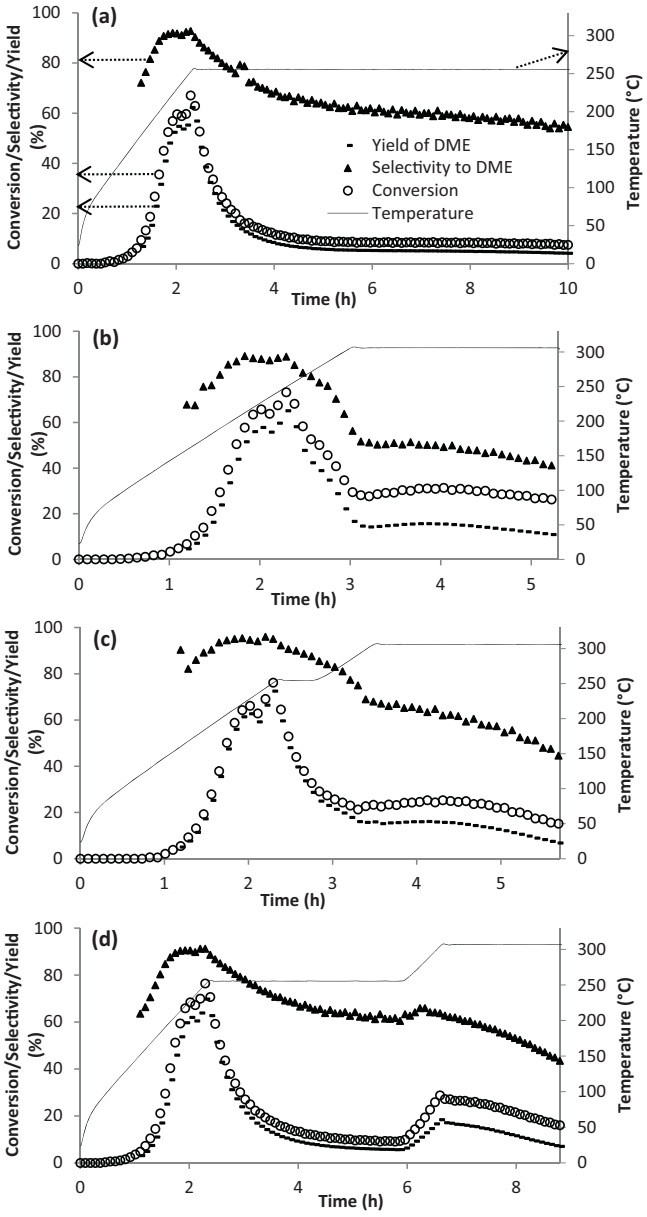


**Fig. 4.** Conversion of methanol, selectivity to DME and yield of DME as a function of time following four different temperature programs containing either one single (a–b) or two successive (c–d) reaction phases at constant temperature (250 °C in (a), 300 °C in (b), and both successively in (c–d) with varying durations from (c) to (d)). Same conditions as for Fig. 1: 30 mg HPW12, total inflow of 60 mL/min (nitrogen saturated with 10 vol.% of methanol).

from 90% at the start to 60% at the end. Then, at 300 °C, it further decreases continuously towards a final value of 45% at the end of the test.

As considering now the conversion data of Figs. 4b/c/d and of Fig. 1 all together, the following trends appear.

First, depending on the time spent at 250 °C (0–1 min on Fig. 4b <30 min on Fig. 4c <2 h on Fig. 1 <3.5 h on Fig. 4d), the heating from 250 to 300 °C has a different impact: either it makes the conversion drop (after short times at 250 °C, Figs. 4b/c), or it makes the conversion rise up again (after long times at 250 °C, Figs. 1 and 4d). In any case, the resulting conversion upon reaching 300 °C is always about the same (26–30%). Knowing that the total number of HPW12's protons is constant from 25 °C up to 350 °C (3 per Keggin unit)[8], this suggests that, whatever the time spent at 250 °C within an interval of 3.5 h, there is always a precise/fixed number of protons being still active (not yet capped within coke molecules) upon reaching 300 °C. In other words, knowing that coking occurs permanently both at 250 °C and upon heating to 300 °C (see e.g. Figs. S7/S8 evaluating the yields of coke with time-on-stream associated respectively to Fig. 4a/b), there is a maximum number of protons above which coking/deactivation does no longer affect the conversion obtained upon reaching 300 °C. Depending on whether this maximum number is already reached or not within the time spent at 250 °C, the heating to 300 °C has or has not to finish the job, and makes thus respectively the conversion drop (as the further loss of active protons prevails over the temperature-induced increase of activity/proton) or rise (as only the temperature-induced activity/proton increase occurs) from its final value at 250 °C to its initial 26–30% at 300 °C.

Second, the time spent at 250 °C determines the time during which the 26–30% conversion at 300 °C remains stable before finally decreasing towards 0. Precisely, the less time is spent at 250 °C, the longer the 26–30% conversion at 300 °C is stable (35 min of stability on Fig. 4d <60 min on Fig. 1 <82 min on Fig. 4c < at least 2.5 h on Fig. 4b). This suggests that the number of protons mentioned above as being still active (not yet capped within coke molecules) upon reaching 300 °C is actually higher than the minimum number required to achieve the 26–30% conversion at 300 °C. In other words, there is an excess of still active protons remaining upon reaching 300 °C. The less time is spent at 250 °C, the larger the latter excess is and the longer it takes to deactivate it at 300 °C.

The nature of the just mentioned excess of protons will be discussed in Section 3.3. At this stage, the catalytic behavior at 250 and 300 °C after having heated HPW12 from 25 °C under methanol (thus after having applied the bulk activation procedure) can be summarized as follows. The conversion first rapidly drops, then it abruptly stops dropping and remains stable for a certain time (depending on the reaction temperature – 250 or 300 °C – and on the time that has already been spent below that reaction temperature), and finally it slowly decreases again. Regarding the selectivity to DME, it always drops when the conversion does so, and when the conversion is stable, it still decreases but much slower (what implies then a relatively stable yield of DME). In other words, when the reaction is launched through the bulk activation procedure, there is a break in the deactivation of HPW12 in which the latter keeps on producing DME with a significant yield (5% at 250 °C and 15–17% at 300 °C, in the here used conditions), and this break lasts for a significant time (5 h at 250 °C and 35 min to 2.5 h at 300 °C, in the here used conditions).

### 3.2. Reaction without passing through the bulk activation procedure

Fig. 5 shows the conversion of methanol, the selectivity to DME and the yield of DME as a function of time at 250 °C (Fig. 5a) and at 300 °C (Fig. 5b) after heating 30 mg of HPW12 from 25 °C under pure nitrogen (reaction still with 10 vol.% of methanol in nitrogen, total inflow of 60 mL/min). So, in these two experiments, HPW12 is exposed to methanol only once the reaction temperature is reached, not from 25 °C, what directly implies [13] that the reaction takes place exclusively at the surface, not within the bulk. Figs. S9/S10 in the Supplementary Information show the selectivities to byproducts and the yield of coke (evaluated as described in Section 3.1) associated respectively to Fig. 5a/b.

At 250 °C (Fig. 5a), the conversion has an initial value of 64%. Then, it immediately drops. After 30 min, it is already down at 6.5%. From 1 to 1.5 h, it is less than 2%. From 1.5 h to the end of the test, it is nearly 0. So, in contrast to what was observed on Fig. 4a in Section 3.1, there is no break in HPW12's deactivation here. In other words, the deactivation is much faster here (with only about 1 h of significant conversion here vs 7.5 h on Fig. 4a). Regarding the selectivity

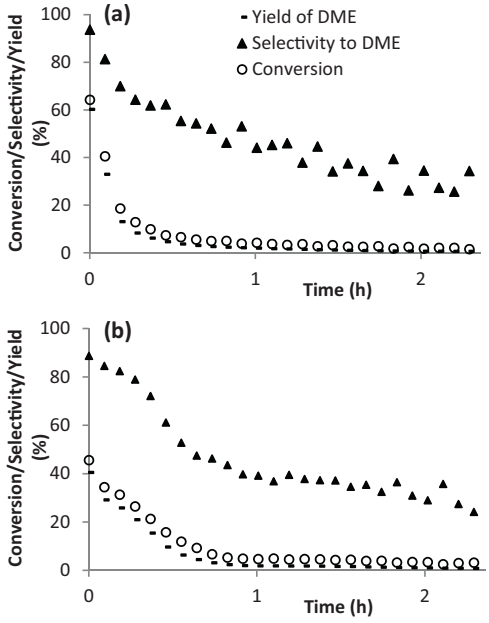


**Fig. 5.** Conversion of methanol, selectivity to DME and yield of DME as a function of time at (a) 250 °C and (b) 300 °C, after heating from 25 °C under pure nitrogen. Same conditions as for Figs. 1 and 4: 30 mg HPW12, total inflow of 60 mL/min (nitrogen saturated with 10 vol.% of methanol).

to DME, it continuously drops from 93% at the start to 25–35% at the end of the test (the fluctuations from 1 h being attributed to the high error at low conversions). In an additional experiment (not shown), the HPW12-methanol system has been heated to 300 °C after 3.5 h of reaction at 250 °C (equivalent to the experiment of Fig. 4d in Section 3.1). The conversion remained however at the same level as observed here from 1.5 h on Fig. 5a (instead of rising as observed on Fig. 4d).

At 300 °C (Fig. 5b), the conversion again immediately drops, this time from an initial value of 46% (lower than at 250 °C, likely because the true initial conversion dropped so fast that the GC could not catch it within the first injection). After 30 min, it is already down at 15%. From 1 h, it is less than 4%. Exactly as at 250 °C, the selectivity to DME continuously drops, from 88% at the start to 24% at the end of the test (the yield of DME being nearly 0 already from 1 h of reaction). So, again, HPW12′s deactivation is much faster here than in the equivalent experiment in Section 3.1 (see Fig. 4b showing still 26% of conversion and 11% of DME yield at the end of the test, namely after having already been active for 4.5 h, including the period of activity during the heating from 25 °C).

So, when HPW12 has not been pre-treated with the bulk activation procedure, the conversion at 250–300 °C permanently and rapidly drops until reaching a negligible value, instead of first rapidly dropping to a certain level, then making a long break, and finally dropping again as observed in Section 3.1. As a consequence, HPW12 gets deactivated much faster (about 8 and 5 times faster respectively at 250 and 300 °C, if considering the yield of DME).

### 3.3. The role of the bulk

The activity observed during the deactivation breaks in Section 3.1 (Figs. 1 and 4) is due to the bulk of HPW12. Indeed, it is not observed when the reaction is limited to the only surface (Fig. 5 in Section 3.2). Moreover, this activity increases when the particle size decreases, what shows that it is limited by internal diffusion (an additional experiment equivalent to the one on Fig. 4b has been performed with particles <100 μm, not shown). Actually, this internal diffusion limitation is precisely the reason for the deactivation breaks, as reflected by the TGA results after the catalytic tests. Indeed, as shown on Fig. 6, after 2.5 h of reaction at 300 °C, the first sample of which the bulk had been activated (performance shown on Fig. 4b) shows a 2 times higher weight-percentage of coke than the second one of which the bulk had not been activated (performance shown on Fig. 5b) (see Fig. S11 for the raw TGA profiles). However, in contrast to the second one, the first sample was still active at the end of the test, and still with the same performance as at the start of the 300 °C plateau. So, the additional coke within the first sample, that can have accumulated only within its bulk, has not induced any decrease of activity. This means that the sites on which it has accumulated were actually not required for the observed performance. Indeed, as long as the latter is limited by internal diffusion, it means that there is an excess of active sites compared to the amount of methanol that is able to enter/diffuse in the bulk, and that deactivating a part of these sites is not a problem (there are still enough sites remaining to maintain the same activity). The activity remains thus stable, until all of the bulk's protons have been solicited/deactivated (see the final conversion decrease after the deactivation breaks on Figs. 1 and 4c/d).

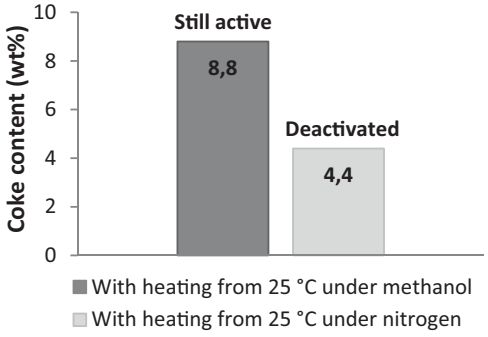


**Fig. 6.** Coke content (wt%) of HPW12 after 140 min of methanol reaction at 300 °C as a function of the gas flow composition during the prior heating from 25 °C ("under methanol" meaning actually "under 10 vol.% of methanol in nitrogen").

So, depending on its pre-treatment, one and the same HPW12 sample 100–200 μm used in the methanol-to-DME process at 300 °C can get deactivated within less than 1 h (surface-type reaction) or remain active (with a yield of DME that is significant and adjustable via the sample mass) for more than 4 h (bulk-type reaction, as including the period of heating from 25 °C). The fact that, in spite of internal diffusion limitations, the lifetime gained thanks to the bulk is provided with a significant yield of DME is due to the enormous fraction of acid sites that the bulk contains. Indeed, with a surface area of 5 $m^2/g$ (measured through the physisorption of nitrogen which, being nonpolar, does not enter the bulk) [20], HPW12 contains 96% of its weight/protons within its bulk (if assuming that Keggin units are spherical and have a diameter of 1 nm) [21].

The precise way to interpret the activity profile observed on Fig. 1 in the temperature programmed reaction from 25 to 350 °C is now clear as well. The immediate drops of conversion upon reaching 200 and 250 °C are due to the coking/deactivation of HPW12's surface, whereas the drop after 1 h of stability at 300 °C is due to the coking/deactivation of HPW12's bulk (after the latter having been itself responsible for the rise of conversion upon heating from 250 to 300 °C, a stage at which the surface was almost completely deactivated already).

## 4. Conclusions

When using HPW12 as catalyst in the methanol-to-DME reaction at 250–300 °C, namely under coking conditions, passing through the bulk activation procedure – consisting of dehydrating

HPW12 and pre-exposing it to methanol at 25 °C before heating it to the reaction temperature – is crucial. Indeed, the bulk remains accessible once the surface is coked/deactivated. However, it contains 24 times more acid sites than the surface, and internal diffusion limitations prevent these sites from being active all at the same time. As a consequence, after deactivation of the surface, a significant activity is maintained for a significant time before the catalyst bed gets definitely deactivated. Actually, during the latter time, the bulk contains continuously enough fresh protons being able to take over the job of the other bulk protons that are deactivated (in the sense that they are capped within coke molecules). In other words, pre-activating the bulk of HPW12 allows significantly increasing the latter's lifetime.

Actually, as HPW12 gets fully exploited here until the last of its available bulk protons has contributed to the reaction, one may no longer state that using unsupported Keggin HPAs necessarily implies the wastage of acid sites. Indeed, such a wastage only comes up when the bulk has not been pre-activated. In the latter case, HPW12 gets indeed deactivated after having solicited only 4% of its acid sites, with the other 96% being simply lost.

Furthermore, this work gives the guidelines on how to interpret the general activity profile obtained upon submitting HPW12 to a temperature programmed reaction of methanol from 25 to 300 °C with relatively short dwell times (2 h here). Indeed, at low temperatures, if the time spent is not sufficient, only the surface gets deactivated. As a consequence, the bulk being still active, a subsequent heating to higher temperatures makes the conversion rise up again instead of further dropping. Then, the ultimate conversion drop only occurs once the bulk is in turn fully deactivated.

Finally, this work shows that one has to be careful in relating the lifetime of a Keggin HPA to the amount of coke it accumulates. Indeed, the amount of coke that the HPA is able to accumulate before getting deactivated depends on whether its pre-treatment included or not the activation of its bulk. In other words, the samples with the highest amount of coke are not the ones which have been the most rapidly deactivated here.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2017.03.034.

## References

[1] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171–198.
[2] M.J. Janik, K.A. Campbell, B.B. Bardin, R.J. Davis, M. Neurock, Appl. Catal. A: Gen. 256 (1–2) (2003) 51–68.
[3] A. Bielański, A. Lubańska, A. Micek-Ilnicka, J. Poźniczek, Coord. Chem. Rev. 249 (21–22) (2005) 2222–2231.
[4] R.M. Ladera, M. Ojeda, J.L.G. Fierro, S. Rojas, Catal. Sci. Technol. 5 (1) (2015) 484–491.
[5] W. Alharbi, E.F. Kozhevnikova, I.V. Kozhevnikov, ACS Catal. 5 (12) (2015) 7186–7193.
[6] Y. Fu, T. Hong, J. Chen, A. Auroux, J. Shen, Thermochim. Acta 434 (1–2) (2005) 22–26.
[7] F. Yaripour, F. Baghaei, I. Schmidt, J. Perregaard, Catal. Commun. 6 (2) (2005) 147–152.
[8] I.V. Kozhevnikov, J. Mol. Cat. A: Chem. 262 (1–2) (2007) 86–92.
[9] A. Micek-Ilnicka, J. Mol. Catal. A: Chem. 308 (1–2) (2009) 1–14.
[10] S. Akaratiwa, H. Niiyama, J. Chem. Eng. Jpn. 23 (2) (1990) 143–147.
[11] A. Małecka, J. Poźniczek, A. Micek-Ilnicka, A. Bielański, J. Mol. Catal. A: Chem. 138 (1) (1999) 67–81.
[12] R.M. Ladera, J.L.G. Fierro, M. Ojeda, S. Rojas, J. Catal. 312 (2014) 195–203.
[13] J. Schnee, E.M. Gaigneaux, Catal. Sci. Technol. 7 (2017) 817–830.
[14] L. Nakka, J.E. Molinari, I.E. Wachs, J. Am. Chem. Soc. 131 (2009) 15544–15554.
[15] J. Schnee, E.M. Gaigneaux, Spectrochim. Acta Part A 173 (2017) 151–159.
[16] Q. Qian, J. Ruiz-Martínez, M. Mokhtar, A.M. Asiri, S.A. Al-Thabaiti, S.N. Basahel, B.M. Weckhuysen, Catal. Today 226 (2014) 14–24.
[17] Y.T. Chua, P.C. Stair, J. Catal. 213 (1) (2003) 39–46.
[18] R.W. Court, M.A. Sephton, J. Parnell, I. Gilmour, Geochim. Cosmochim. Acta 71 (10) (2007) 2547–2568.
[19] O. Beyssac, B. Goffé, J.-P. Petitet, E. Froigneux, M. Moreau, J.-N. Rouzaud, Spectrochim. Acta Part A 59 (10) (2003) 2267–2276.
[20] T. Sugii, R. Ohnishi, J. Zhang, A. Miyaji, Y. Kamiya, T. Okuhara, Catal. Today 116 (2) (2006) 179–183.
[21] Z. Karimi, A.R. Mahjoub, S.M. Harati, Inorg. Chim. Acta 376 (1) (2011) 1–9.