"Supporting the Dawson (NH4)6P2Mo18O62 heteropoly compound: controlling its molecular behaviour to enhance its catalytic activity in the propene oxidation"

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ABSTRACT

This paper shows how supporting the Dawson heteropoly compound (HPC) (NH4)6P2Mo18O62 opens up the possibility to enhance its catalytic activity by controlling its molecular behaviour. The effect of parameters such as the loading of the Dawson species onto a support and the nature of its interaction is explored by IR and Raman spectroscopy and correlated with its performance in the oxidation of propene. Active species in propene oxidation were formed during the Dawson HPC rearrangement occurring on a TiO2 support. When supported, the Dawson (NH4)6P2Mo18O62 HPC is beneficially activated during the catalytic process, which led to the formation of a supported active species. A conversion stability observed for the HPC/TiO2 samples with loading above 5 wt.-% revealed that the Dawson HPC had to interact with the support to develop a stable activity. This arrangement seemed indeed to be the most suitable to reach a high conversion. On the contrary, it was proposed that isolated HPC species ...

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Supporting the Dawson (NH₄)₆P₂Mo₁₈O₆₂ Heteropoly Compound: Controlling Its Molecular Behaviour to Enhance Its Catalytic Activity in the Propene Oxidation

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Keywords: Heteropoly compounds / In situ characterization / Oxidation / Dawson / Supported catalysts / Molybdenum

This paper shows how supporting the Dawson heteropoly compound (HPC) (NH₄)₆P₂Mo₁₈O₆₂ opens up the possibility to enhance its catalytic activity by controlling its molecular behaviour. The effect of parameters such as the loading of the Dawson species onto a support and the nature of its interaction is explored by IR and Raman spectroscopy and correlated with its performance in the oxidation of propene. Active species in propene oxidation were formed during the Dawson HPC rearrangement occurring on a TiO₂ support. When supported, the Dawson (NH₄)₆P₂Mo₁₈O₆₂ HPC is beneficially activated during the catalytic process, which led to the formation of a supported active species. A conversion stability observed for the HPC/TiO₂ samples with loading above 5 wt.-% revealed that the Dawson HPC had to interact with the support to develop a stable activity. This arrangement seemed indeed to be the most suitable to reach a high conversion. On the contrary, it was proposed that isolated HPC species were more prone to destabilization due to the loss of the proximity between the anions in the HPC crystal lattice. This work will show that the catalytic systems operated very efficiently due to the redox properties of molybdenum atoms when in an HPC 3D framework. This could not have happened with low loadings as only fragments of the HPCs were present on the surface. The stabilization of catalytic activities observed in the supported catalysts with high loadings was associated with the stabilization of a Keggin-like supported phase.

1. Introduction

Heteropoly compounds (HPCs) are polyoxometalates incorporating heteropolyanions ([XₘMₙOₙ₊q]: X = P, Si, ...; Mₙ = Mo, W, V, ...) and a counter cation (H⁺, NH₄⁺, K⁺, ...). HPCs are receiving interest in catalysis as they present tunability at several levels: (i) their formulation (possible substitutions of addenda atoms and countercations), (ii) their structure (Keggin = PMo₁₂O₄₀⁻, Dawson = P₂Mo₁₈O₆₂⁻, etc.) and (iii) their ability to rearrange with thermal treatment.

Previous researchers have shown that (NH₄)₆P₂Mo₁₈O₆₂ HPCs are promising heterogeneous catalysts for oxidation reactions.[2-4] Bulk (NH₄)₆P₂Mo₁₈O₆₂ HPCs may, along its thermal decomposition path, indeed generate more active species. As an example, the highest activity observed with bulk (NH₄)₆P₂Mo₁₈O₆₂, for the 2-butanol catalytic oxidation was obtained on a “living” catalyst, formed in situ, likely with a wobbly structure.[2] These previous contributions have shown that the thermal rearrangement of the Dawson (NH₄)₆P₂Mo₁₈O₆₂ heteropoly compound catalyst is beneficial for the catalytic activity. Dawson (NH₄)₆P₂Mo₁₈O₆₂ HPC is indeed beneficially activated during the catalytic processes, which leads to the formation of active sites performing the catalytic work. However, we have not succeeded in stabilizing the most active state for a long time, observing a continuous deactivation with time-on-stream. Working under adequate conditions to maintain the most active intermediate could be the most promising way to take advantage of HPCs.

Our recent studies demonstrated that the adjustment of the redox strength of the gaseous feed is a way to control the reorganisation of a Dawson (NH₄)₆P₂Mo₁₈O₆₂ salt.[3,4] It was used in particular to modulate the catalytic activities of the (NH₄)₆P₂Mo₁₈O₆₂ catalyst in the propene oxidation.[3,4] In this contribution, we will investigate another way to regulate the Dawson (NH₄)₆P₂Mo₁₈O₆₂ reorganisation. We therefore investigated the supported Dawson (NH₄)₆P₂Mo₁₈O₆₂ HPC. The strategy is to study the stabilizing effect that supporting HPCs could bring to the rearrangement of the Dawson (NH₄)₆P₂Mo₁₈O₆₂ HPC. The possibility of designing different supported species as a function of the Dawson (NH₄)₆P₂Mo₁₈O₆₂ HPC loadings will also be investigated. Moreover, the catalytic behaviour of the supported Dawson (NH₄)₆P₂Mo₁₈O₆₂ heteropoly compound was investigated under real catalytic conditions through the oxidation of propene. Propylene oxidation produces mainly acrolein, which is an essential precursor of other important compounds like amino acids or acrylic acids. Even though our supported (NH₄)₆P₂Mo₁₈O₆₂ HPC turned out to be less selective than we had hoped we will...
investigate why this catalyst is active for the total propene oxidation, which will indirectly help to further improve this family of catalysts.

Contradictory opinions exist about the thermal stability of supported HPCs as a function of the type of HPC and support.\textsuperscript{[5–7]} For instance, some authors have found that the thermal stability of HPCs decreases when they are supported.\textsuperscript{[5–7]} Other authors inferred that supported HPCs keep their structures intact up to a higher temperature than the bulk parents.\textsuperscript{[8]} P. Vazquez et al. report that \(H_3^+PMO_{12}O_{40}\) stays mainly undegraded up to 250, 400 and 500 °C when supported on alumina, titania and silica, respectively, while the bulk compound remains stable up to 450 °C.\textsuperscript{[5]} In the same way, Damyanova et al. report that silica enhances the thermal stability of \(H_3^+PMO_{12}O_{40}\) compared to that of the bulk, while the mixed \(ZrO_2–SiO_2\) support leads to a destruction of \(H_3^+PMO_{12}O_{40}\) due to its stronger interaction with zirconia.\textsuperscript{[7]} On the contrary, Rocchiccioli-Deltcheff et al. report that a silica support induces destabilization of 12-molybdophosphoric acid.\textsuperscript{[6]}

Moreover, literature reports that silica- and titania-supported HPCs preserved their Keggin structure.\textsuperscript{[8]} The latter is unaffected by the support, and the catalytic oxidation used at 400 °C did not destroy the heteropoly anion structure.\textsuperscript{[8]} Damyanova et al. also came to the conclusion that the Keggin structure was not perturbed by a titania support.\textsuperscript{[9]} On the contrary, Keggin structures on alumina supports are destroyed as a result of their contact with basic centres of the surface.\textsuperscript{[8]} The relatively poor stability of HPC on alumina suggests that more acidic supports are favourable.\textsuperscript{[10]} Sopa et al. indeed explained that the oxidative activity of \(H_3^+PMO_{12–x}V_xO_{40}/SiO_2\) and \(H_3^+PMO_{12–x}V_xO_{40}/\)TiO\(_2\) was due to the presence of heteropoly anions of regular or defected structures, while the oxidation of \(H_3^+PMO_{12–x}V_xO_{40}/Al_2O_3\) resulted from the formation of mixed Mo–V–P oxides on the alumina surface.\textsuperscript{[8]} Thus, the main point raised by the literature is the following: an adapted support could be used to destabilize the HPC unit with the simultaneous stabilization of the effective active species.\textsuperscript{[6,11]} The isoelectric point of the solid surfaces was estimated at about 2.2, 5.6 and 8.1 for SiO\(_2\), TiO\(_2\) and Al\(_2O_3\), respectively.\textsuperscript{[8]} Titania is thus a support with intermediate (quasi neutral) surface in comparison to silica and alumina. We thus hope that titania possesses this peculiar influence.

This aspect was the main objective of this research: the use of HPCs as molecular precursors of supported active species in the propene oxidation. Keggin-type heteropoly compounds are commonly found to be more stable than Dawson-type heteropoly compounds and thus, a priori, are more able to perform oxidation reactions. Nevertheless, in this project, Dawson catalysts are chosen as starting catalysts, because they are less stable than Keggin ones and thus more prone to rearrangement. As a consequence, with Dawson compounds it could be easier to reach our objective, and these compounds have been treated here as promising precursors of active species. As a continuation to our previous research,\textsuperscript{[2–4]} the ammonium salt \((NH_4)_6P_2^+ \cdot \text{Mo}_{18}O_{40}\) was chosen as the starting catalytic material and was supported on TiO\(_2\). The activity of \((NH_4)_6P_2\text{Mo}_{18}O_{40}/\)TiO\(_2\) in propene oxidation was evaluated at 300 °C over 6 h. We inferred that the titania support favours the formation and stabilization of the active species at a lower temperature than previously observed for bulk HPCs (350–400 °C).\textsuperscript{[5]}

2. Results

2.1. Characterizations of Freshly Supported Samples

2.1.1. Infrared and Raman Spectroscopic Analyses

The main IR and Raman spectroscopic features of \((NH_4)_6P_2\text{Mo}_{18}O_{40}\) were observed in the TiD\(_24\) and TiD\(_{14}\) spectra. The IR spectroscopic features of \((NH_4)_6P_2\text{Mo}_{18}O_{40}\) are shown in Figure 1(b) and (c). The signals at ca. 1077 and 908 cm\(^{-1}\) and at ca. 1002 and 940 cm\(^{-1}\) are characteristic of those for the central phosphorus species \(\nu_{as}(\text{P}–\text{O}a)\) and \(\delta(\text{Oa–P}–\text{Oa})\) and the Mo–O species in the phosphomolybdic Dawson structure \(\nu_{as}(\text{Mo–Od})\) and \(\nu_{as}(\text{Mo–Oc–Mo})\) edge sharing, respectively.\textsuperscript{[12,13]} In addition, the IR spectra show an infrared signal for the \(NH_4^+\) species at 1403 cm\(^{-1}\). Raman vibrations at 971 and 711 cm\(^{-1}\), attributed to the stretching mode of the terminal Mo–Od and to the Mo–O–Mo stretching\textsuperscript{[13]} are seen in Figure 2(b) and (c). These IR and Raman spectroscopic features confirm the presence of undegraded heteropoly compounds in the impregnated samples.

![Figure 1](image_url)

Figure 1. IR spectra of (a) D, (b) TiD\(_{24}\), (c) TiD\(_{14}\), (d) TiD\(_5\), (e) TiD\(_2\) and (f) Ti. IR bands of the \(P_2\text{Mo}_{18}O_{40}\) anion (plain lines) and of \(NH_4^+\) (dotted line). The broad band in the 400–800 cm\(^{-1}\) zone was attributed to titania.\textsuperscript{[8]}

Subtraction of the IR spectrum of the support from the supported samples revealed that for TiD\(_{24}\) there was a shift of the Mo–O–Mo corner-sharing vibration to higher frequencies [Figure 3(b), peaks shown with *]. This indicated that some of the O atoms from the heteropoly compound
interacted with the support. Other O atoms did not directly come into contact with the support resulting in unchanged vibration frequencies [Figure 3(b), bands shown with °]. This second IR band was not observed in the TiD14 IR spectrum [Figure 3(c)] suggesting that, at low loading, all Dawson species were in contact with the support. Such a result was in accordance with the study of Pozniczek et al. on \( \text{H}_3\text{P}_2\text{W}_{18}\text{O}_{62} \) supported on TiO\(_2\) and SiO\(_2\).[14] An interaction of the Dawson structure with the support was observed with TiD14. However, this interaction was weak: the solute/support interaction followed the decreasing order: alumina, carbon, silica and titania.[5] A marked interaction would have led to the loss of the tetrahedron symmetry and a broadening of the band attributed to the stretching frequency (at 1077 cm\(^{-1}\)) of the PO\(_4\) tetrahedron, as observed in \( \text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \) supported on SiO\(_2\) because of the interaction of the WO\(_6\) octahedra with the silanol groups.[15] This was clearly not observed here.

The identification of the Dawson heteropoly compound was difficult in TiD5 and TiD2. The intensities of the IR and Raman bands characteristic of the Dawson anion decreased as a function of the loading [Figure 1(d) and (e) and Figure 2 (d) and (e)]. However, the Raman vibration of the terminal Mo–O group in the Dawson anion was observed at a lower frequency in the TiD5 and TiD2 spectra (950 cm\(^{-1}\)) than in the D spectrum (976 cm\(^{-1}\)) [Figure 2(a), (d) and (e)]. This was also observed in TiD24 and TiD14 but to a lesser extent [Figure 2(b) and (c)]. Rocchiccioli-Deltcheff et al. also observed that impregnation of \( \text{H}_3\text{PMo}_{12}\text{O}_{40} \) on silica induced a decrease in the Mo–Od frequency.[8] The frequency of Mo–O was high in the bulk compound because of the proximity of the polyanions in the crystal lattice (anion–anion interactions). Rocchiccioli-Deltcheff et al. explained that decreasing the concentration of the deposit on the support induced a weakening of these interactions, which could be neglected at low coverage: as a consequence, the frequency decreased.[6] This suggested that there was a low coverage of the surface in our TiD5 and TiD2 samples.

Moreover, the band assigned to the Mo–O–Mo stretching vibration almost disappeared in the Raman spectra of TiD5 and TiD2 [Figure 2(d) and (e)]. It might indicate the breaking of the Mo–O–Mo bond on the TiO\(_2\) surface and, hence, that only a defective Dawson structure remained on the TiO\(_2\) support. This was already observed for heteropoly compounds supported on SiO\(_2\) at low loading and interpreted to be a result of the strong interaction with the silanol groups.[11]

### 2.1.2. X-ray Diffraction Analysis

Distinct diffraction peaks of heteropoly compounds were not seen in the XRD patterns of the supported samples [Figure 4(b)–(e)], indicating that the Dawson species were molecularly well dispersed over the surface of TiO\(_2\) and did not form crystalline species or large particles. Only the XRD lines of TiO\(_2\) were found on the patterns of the supported samples.

### 2.1.3. Elemental and XPS Analyses

The Mo/P ratios found by ICP were equal to the theoretical Mo/P ratio in the Dawson heteropoly compound (Table 1) The ratios determined by XPS were lower than the bulk Mo/P ratios for TiD24, TiD14, TiD5 and TiD2. The ratio of Mo/Ti decreased as a function of the Dawson loading.

The values of the binding energies for Mo 3d 5/2 suggested that the Mo atom was reduced when the Dawson compound was supported on TiO\(_2\) (Figure 5). Mo\(^{5+}\) was clearly visible on TiD2 (BE Mo 5/2 of 231.4 eV). This could have been caused by an electron transfer between molybdenum and titania or by a change in the coordination
Supporting the Dawson (NH₄)₆P₂M₀₁₈O₆₂ Heteropoly Compound

2.2. Catalytic Activity

The bulk Dawson sample and TiO₂ support were inactive during the oxidation of propene at 300 °C. The propene conversion stabilized at 64%, 69% and 60% for TiD24, TiD14 and TiD5, respectively, after approximately 1 h of testing, and remained stable at 300 °C for 6 h and then decreased with the temperature (Figure 6). CO and CO₂ were the main products. Intense releases of heat were observed for all three tests (the reactor temperature was higher than the oven temperature). The lowest propene conversion was observed for TiD2 [Figure 6(d)]. In contrast to the stable level of conversion observed with 5%, 14% and 24% of loading, a decrease of activity was noted with time-on-stream with 2% of loading. This decrease could have reflected a deactivation of the TiD2 catalyst with time. This aspect will be discussed below. The specific activity evolution of the propene oxidation of the samples with time-on-stream is shown in Figure 7. The following order was found: TiD5 \( > \) TiD2 \( > \) TiD14 \( > \) TiD24. The best activity was thus obtained with TiD5.

2.3. Post-Test Characterizations

2.3.1. Infrared and Raman Analyses

After catalysis, the D and TiD24 samples showed typical IR spectra of Keggin compounds [Figure 8(a) and (b)]. IR analyses, however, showed differences between the bulk and supported tested samples. For instance, the N–H vibration at 1400 cm⁻¹ did not appear in the IR spectra of the supported samples [Figure 8(b)–(e)]. Keggin bands at 1063 and 963 cm⁻¹ were also observed in the TiD14 spectrum [Figure 8(c)]. A broad band centred at 1090 cm⁻¹ appeared in the TiD5 IR spectrum [Figure 8(d)]. This could have been the vibration of the P–O bond whose IR position shifted number of molybdenum due to the formation of different types of bonds with the support, as reported in ref.[9] The binding energies of P 2p 3/2 for supported samples suggested the presence of P⁵⁺ ions in all of the samples (Table 2). No chloride was found on the supported Dawson samples.

Table 2. XPS intensity ratios (Mo/P and Mo/Ti) and binding energies of Mo and P of D, TiD24, TiD14, TiD5 and TiD2 before and after testing at 300 °C.

<table>
<thead>
<tr>
<th></th>
<th>Mo/P</th>
<th>Mo/Ti</th>
<th>Mo 3d 5/2 [eV]</th>
<th>P 2p 3/2 [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>8.4</td>
<td>–</td>
<td>233.4</td>
<td>133.9</td>
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<tr>
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<td>0.28</td>
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<td>133.7</td>
</tr>
<tr>
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<td>0.2</td>
<td>233.1</td>
<td>133.8</td>
</tr>
<tr>
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<td>0.15</td>
<td>233.1</td>
<td>133.9</td>
</tr>
<tr>
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<td>0.06</td>
<td>231.4</td>
<td>133.1</td>
</tr>
<tr>
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<tr>
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</tr>
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<td>TiD2-tested</td>
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<td>0.06</td>
<td>232.6</td>
<td>133.2</td>
</tr>
</tbody>
</table>
Figure 6. Catalytic performance of the (a) TiD24, (b) TiD14, (c) TiD5 and (d) TiD2. Reactor (plain line) and oven (dotted line) temperatures. Conversion of propene (full dots) and selectivities in acrolein (empty dots), acetaldehyde (empty triangles) and CO/CO₂ (full triangles). For the sake of clarity, we decided to limit the amount of presented data to 25% of the originally acquired ones.

Figure 7. Specific activity as a function of time for (a) TiD5, (b) TiD2, (c) TiD14 and (d) TiD24.

to a wavenumber higher than its initial position in the IR spectrum of HPC. On the one hand, the broadening of the IR band could have been due to the loss of tetrahedron symmetry because of the interaction between HPC and the support as mentioned in ref.[15] On the other hand, the shift to a higher frequency could be due to the fact that the P–O bonds interacted with the support. These two facts meant that the HPC is completely destroyed after testing and that the remaining fragments interacted with the support. In a complete HPC, the P–O bonds were in the central position of the HPC unit and were thus preserved from interaction with the environment. If the HPC had remained intact after the test, the interaction with the support could not have induced the shift of the IR vibration of the HPC P–O bonds, as observed in our case. This argued in favour of the presence, after the tests, of a destroyed HPC.

The transformation of the Dawson heteropoly compound into the Keggin compound was confirmed by Raman spectroscopy: bands at 980, 965, 874, 604 and 238 cm⁻¹ were observed for the tested bulk sample [Figure 9(a)]. The Raman signals of the supported samples were more complex. A band appeared at 814 cm⁻¹ for TiD24 and TiD14 [Figure 9(b) and (c)], which could be related to the Mo–O–Mo vibration as observed in MoO₃.[16] A broadening of the
Supporting the Dawson (NH₄)₆P₂Mo₁₈O₆₂ Heteropoly Compound

Figure 8. IR spectra obtained for (a) D, (b) TiD₂₄, (c) TiD₁₄, (d) TiD₅, (e) TiD₂ and (f) Ti after testing at 300 °C. IR bands of the PMo₁₂O₆₀ anion (plain lines) and of NH₄⁺ (dotted line).

A band characteristic of the Mo–Od vibrations was observed. This band was centred at ca. 990 cm⁻¹, i.e. a higher frequency than the same vibration for the bulk sample. This could be the sign for the departure of the counterion NH₄⁺ during the testing procedure of the supported samples.

Figure 9. Raman spectra obtained for (a) D, (b) TiD₂₄, (c) TiD₁₄, (d) TiD₅, (e) TiD₂ and (f) Ti after testing at 300 °C. The bands at 396, 516 and 638 cm⁻¹ are attributed to the TiO₂ support.[23]

2.3.2. X-ray Diffraction Analysis

The formation of a Keggin structure during catalysis was confirmed by an XRD analysis. D clearly displayed the Keggin (NH₄)₃PMo₁₂O₆₀ pattern [Figure 10(a)]. However, as far as the fresh samples were concerned, only the diffraction lines of TiO₂ were found in the XRD patterns of the supported samples after the test [Figure 10(b)–(e)].

2.3.3. XPS Analysis

The XPS Mo/Ti ratios increased after testing the HPC/Ti samples, suggesting a higher dispersion of molybdenum species on the catalyst surface or the occurrence of clusters breaking up upon testing. This Mo/Ti increase could be related to the rearrangement of the Dawson units in either Keggin or MoO₃ species, as previously shown by IR and Raman spectroscopy and XRD. The number of Mo atoms was indeed proportionally higher in MoO₃ and the Keggin structure (Mo/P = 12:1) than in the Dawson (Mo/P = 18:2) species. The binding energy of Mo 3d 5/2 for the bulk sample clearly decreased after testing, i.e. the bulk sample reduced upon testing, while a reoxidation of the catalysts seemed to happen when they were supported. The TiD₂ clearly reoxidized after the test but still has a lower binding energy than observed in a D fresh sample (Figure 5 and Table 2).

2.3.4. On-Line Characterization

The loss of NH₄⁺ during the tests, as clearly observed in the post-test IR spectra of the supported catalysts, was confirmed by tracking the gaseous products during catalysis by mass spectrometry. Fragments with $m/z = 28$ (corresponding to N₂) and 30 (corresponding to NO and NO₂) were observed for the supported samples (Figure 11 and Figure 12). These fragments are presumably formed by the loss of NH₄⁺ and its instantaneous combustion under oxidation conditions. This was not observed with the bulk Dawson sample. In addition, the supported samples released H₂O ($m/z = 18$ and 17), P ($m/z = 47, 63, 79, 95$ and 142) and Mo ($m/z = 96, 128$ and 144) species. Once again, these behaviours were not observed with the bulk D sample.
Figure 11. MS results of (A) TiD24 and (B) TiD14.

Figure 12. MS results of (A) TiD5 and (B) TiD2.
3. Discussion

3.1. Identity of Freshly Supported Samples

At a high concentration (i.e. 24 and 14 wt.-%) the titania-supported HPC preserved the Dawson structure in the prepared catalysts. IR and Raman spectroscopy revealed the undegraded Dawson HPC as the main species. The lack of a significant vibration frequency shift indicated the absence of any species other than the Dawson heteropoly compound as confirmed by elemental and XPS analyses. Unfortunately, the intensity of the Dawson IR and Raman bands significantly decreased for TiD2 and TiD5 and did not permit a direct identification of the supported species. Moreover, molybdenum was reduced when the Dawson HPC was supported on titania, which was already observed by Predo-eva et al.[17] The binding energy of Mo (Mo$^{5+}$ is clearly observed) as well as P decreased in the TiD2 sample and may be explained in terms of electron-density changes around the P and Mo atoms. Titania support thus affected the Dawson structure.

For high loadings (e.g. 24 wt.-%), based on IR data, there is both (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$ in interaction with the titania support and (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$ aggregates (namely several Dawson HPCs together in the same place) on the support. Multilayers indeed began to form, and analogous species to unsupported (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$ were thus present. For lower loadings, we determined that aggregates of (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$ did not exist and that all Dawson species were strongly interacting with the support surface. At very low loadings (e.g. 2 wt.-%), isolated supported species were thought to be present on the support surface.

3.2. Reorganisation Pathways of the Dawson and Supported Catalysts under Testing

Taking into account the reaction temperature (300 °C), we questioned the pathway of the transformation of the Dawson structure into the Keggin one and its stability.

The tested bulk (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$ Dawson sample showed characteristics of (NH$_4$)$_3$PMo$_{12}$O$_{40}$, whereas (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$ Dawson/TiO$_2$ samples mainly rearranged into H$_3$PMo$_{12}$O$_{40}$ Keggin/TiO$_2$ after testing. The rearrangement was accompanied by the release of ammonium cations, either in the form of N$_2$ or NO$_2$/NO. Two different possibilities in terms of timing of the NH$_4^+$ loss were considered for the supported samples: (i) the (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$ first rearranges into H$_3$P$_2$Mo$_{18}$O$_{62}$, which is then transformed into H$_3$P$_2$Mo$_{12}$O$_{40}$, or (ii) the (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$ is reorganized into (NH$_4$)$_3$P$_2$Mo$_{12}$O$_{40}$, which, afterwards, rearranges into a Keggin acid, namely H$_3$P$_2$Mo$_{12}$O$_{40}$. At this stage it was really difficult to exclude one of the two possibilities.

A previous study showed that the Keggin anion could be transformed, even at 200–250 °C.[4] We could assume that the formed Keggin phase started to decompose during the catalytic test at 300 °C. Rocchicchioli-Delcheff et al. postulated that the collapse of the Keggin H$_3$P$_2$Mo$_{12}$O$_{40}$ was limited thanks to the water formed during the catalytic re-action.[18] These authors explained that H$_3$PMo$_{12}$O$_{40}$ treated at 400 °C (mixture of phosphorus oxide, α-MoO$_3$ and β-MoO$_3$) turned into a mixture of H$_3$PMo$_{12}$O$_{40}$ and α-MoO$_3$ thanks to the water formed during the catalytic reaction:[18] $2$ H$_3$PMo$_{12}$O$_{40}$ $\rightarrow$ P$_2$O$_5$ + 24 β-MoO$_3$ + 3 H$_2$O. Therefore, we inferred that the continuous presence of water vapour in the reaction medium prevented the HPC dehydration and improved the stability of the formed species with features of the Keggin HPC supported on TiO$_2$. The mass spectrometry analyses of the supported samples revealed a vatalitization of P–O and Mo–O species. The IR and Raman analyses also showed the presence of modified P–O and Mo–O–Mo bonds when compared to the bonds inside the heteropoly compound fragments. These results could be related to the presence of both P$_2$O$_5$ and MoO$_3$ and maintained the equilibrium between the Keggin phase and the latter as hypothesized by Rocchicchioli-Delcheff et al. This provided a draft explanation for the stable activities observed (e.g. with TiD24, TiD14 and TiD5 samples) as the active species (with structures related to the Keggin HPC) may be rebuilt after subsequent contact with water vapour. As we have inferred that very defective structures were present as isolated supported species, such an equilibrium would not occur with TiD2. The transformation of the Dawson unit into the Keggin unit would not be straightforward. This provided an explanation for the progressive deactivation observed with time-on-stream for TiD2.

3.3. Towards an Explanation of the Enhancement of the Catalytic Activity in the Supported Samples

As the (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$ bulk sample was inactive in the propene oxidation at 300 °C, the oxidizing activity of the Dawson species (mainly in CO$_2$ products) was enhanced by being dispersed on a titania support. Elements of explanation can be found when considering the TiD2 and TiD5 cases.

In TiD2, the sample with the lowest Mo content, the conversion decreased continuously, showing a trend towards deactivation. Only isolated supported species with reduced molybdenum atoms (Mo$^{5+}$) were present on the TiD2 surface. On the one hand, the deactivation observed could be due to the sole presence of Mo$^{5+}$ on the fresh sample, corresponding to a less favourable distribution of Mo oxidation states for catalysis. On the other hand, isolated species could be more prone to physico-chemical modifications than nonisolated species as on TiD24, TiD14 and TiD5, with a negative effect on the propene conversion of TiD2. The catalytic system operated more efficiently because of the redox properties of molybdenum atoms, which were in the same heteropoly compound framework as TiD2, TiD14 and TiD5, and not in a very defective structure such as TiD2. The highest observed intrinsic conversion for TiD5 could be explained as follows: (i) a more favourable (for catalysis) development of the distribution of reduced molybdenum and oxidized Mo$^{6+}$ sites in the HPC (as observed by XPS in Figure 5), (ii) a more significant
number of surface redox sites than in the TiD24, TiD14 and TiD2 samples because of the better arrangement of species on the surface (monolayer) in TiD5, as discussed previously.

4. Conclusion

In this study, the possibility of using the Dawson (NH₄)₆P₂Mo₁₈O₆₂ heteropoly compound as a precursor of supported active species was explored. In particular, this contribution opens up possibilities for the molecular design of active species by the adjustment of the loadings of the Dawson (NH₄)₆P₂Mo₁₈O₆₂ HPC on the support. The nature of the species stabilized at the TiO₂ surface was highly dependent on the nominal (NH₄)₆P₂Mo₁₈O₆₂ loading. Highly dispersed species are preferentially produced at low loading, while at high loading both (NH₄)₆P₂Mo₁₈O₆₂ in interaction with the support and aggregates of (NH₄)₆P₂Mo₁₈O₆₂, which behave as the nonsupported bulk species, were observed at the surface. (NH₄)₆P₂Mo₁₈O₆₂ HPC/TiO₂ samples with loading above 5 wt.-% developed a stable activity, reaching a propene conversion of up to 69%, thus demonstrating that when only supported species interacting with the support are present, the Dawson (NH₄)₆P₂Mo₁₈O₆₂ heteropoly compound is beneficially activated [bulk (NH₄)₆P₂Mo₁₈O₆₂ heteropoly compounds are not active for propene oxidation]. Isolated species as developed in (NH₄)₆P₂Mo₁₈O₆₂ HPC/TiO₂ samples with loading at 2 wt.-% are more prone to destabilization resulting in a continuous deactivation with time-on-stream.

In addition, the solid-state rearrangement of supported HPCs occurred differently from that of the bulk HPC. Indeed, unlike bulk HPC, the HPC/TiO₂ samples released H₂O, N, P and Mo species, leading to the formation of H₃PMo₁₂O₄₀ Keggin/TiO₂, while the formation of (NH₄)₃P₂Mo₁₂O₄₀ Keggin species was found to occur during the test of bulk HPCs.

Thus, this study highlights the fact that the supporting HPC influences both the Dawson (NH₄)₆P₂Mo₁₈O₆₂ HPC rearrangement and its catalytic activity. TiO₂ was found to simultaneously destabilize the Dawson-supported unit and stabilize the truly active species, with structures related to the Keggin HPC resulting from the Dawson reorganisation. In other words, this contribution indicates the Dawson (NH₄)₆P₂Mo₁₈O₆₂ HPC/TiO₂ precursor role of active supported species.

5. Experimental Section

5.1 Catalyst Preparation

5.1.1 Synthesis of Bulk Dawson HPC: The Dawson salt (NH₄)₆P₂Mo₁₈O₆₂ was synthesized according to Wu[19] as explained in ref[2–4]. The physico-chemical characterization data of this sample has already been presented and discussed in ref[2–4]. The catalyst was denoted as D standing for Dawson HPC.

5.1.2. Synthesis of the Supported Dawson HPC: Supported (NH₄)₆P₂Mo₁₈O₆₂ Dawson HPC samples with loadings between 2 and 24 wt.-% were prepared by wet impregnation. Prior to impregnation, the TiO₂ support (DEGUSSA P25, 49 m²g⁻¹[20,21]) was calcined under static air at 500 °C for 15 h. An appropriate amount of the (NH₄)₆P₂Mo₁₈O₆₂ Dawson HPC (depending on the nominal loading targeted for each synthesis) was diluted in distilled water. The calcined support (7 g) was then suspended in the impregnated solution under magnetic stirring (final volume of 1500 mL) for 2 h. Water was then evaporated under reduced pressure in a rotavapor. Catalysts were denoted as TiDₓ [x represents the nominal weight loading of (NH₄)₆P₂Mo₁₈O₆₂, in wt.-%]. Loadings were checked by ICP-AES (Table 1).

5.2 Catalyst Characterizations: X-ray diffraction (XRD) patterns were recorded with a Siemens DS00 diffractometer by using the Kα radiation of Cu (λ = 0.15418 nm). The 2θ range was scanned between 5° and 80° at a rate of 0.01°s⁻¹. The identification of the phases was achieved by using the ICDD-JCPDS database. Fourier Transformed Infra Red spectra (FTIR) were recorded in the transmission mode by using an IFS55 Equinox spectrometer (Bruker) equipped with a DTGS detector. The spectra were obtained by recording 100 scans between 370 and 4400 cm⁻¹ with a resolution of 4 cm⁻¹. Wafers were prepared after diluting the sample in KBr (Janssens Chimica 99+%) by a weight factor of 100. Raman measurements were carried out with a Thermoscientific DXR Raman microscope (laser of 532 nm, power of 7 mW). The spectra were recorded in the Raman shift range between 100 and 1600 cm⁻¹. The estimated spectral resolution was 6.7–8.3 cm⁻¹, and the acquisition consisted of 10 accumulations for each sample. X-ray photoelectron spectroscopy (XPS) analyses were performed with a Kratos Axis Ultra spectrometer (Kratos Analytical, Manchester, UK) equipped with a monochromatized aluminium X-ray source (powered at 10 mA and 15 kV). The samples were fixed on a standard stainless steel multispecimen holder by using a piece of double-sided insulating tape. The pressure in the analysis chamber was approximately 10⁻⁶ Pa. The pass energy was set at 160 eV for the wide scan and 40 eV for narrow scans. Under the latter conditions, the full width at half maximum (FWHM) of the Ag 3d 5/2 peak of a standard silver sample was about 0.9 eV. Charge stabilization was achieved by using the Kratos Axis device. The following sequence of spectra was recorded: survey spectrum, C 1s, O 1s, Cl 2p, P 2p, Mo 3d, N 1s, Na 1s, Ti 2p and C 1s again to check for charge stability as a function of time and the absence of degradation of the sample during the analysis. The C=(CH) component of the C 1s peak of carbon was fixed to 284.8 eV to set the binding energy scale. The intensity ratio I(Cl 2p 3/2)/I(Cl 2p 1/2) was fixed at 2, with an energy difference of 1.6 eV.[22] The intensity ratio I(P 2p 3/2)/I(P 2p 1/2) was fixed at 2, with an energy difference of 0.84 eV.[22] The intensity ratio I(Ti 2p 3/2)/I(Ti 2p 1/2) was fixed at 2, with an energy difference of 5.54 eV.[22] Decomposition of the Mo 3d doublets was done by fixing as constraints an energy difference of 3.13 eV and an area ratio of 2:3 between the Mo 3d 3/2 and the Mo 3d 5/2 bands.[22] As another constraint, the FWHMs of the two contributions of a doublet were kept identical during the whole decomposition process. Spectra were decomposed with the CasaXPS program (Casa Software Ltd., UK) with a Gaussian/Lorentzian (70:30) product function and after subtraction of a linear baseline. The elemental analysis of the catalysts was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) with the ICAP 6500 Thermo Scientific.

5.3. Catalytic Tests: Catalytic tests were performed in a fixed-bed reactor. Powdered catalysts (400 mg, 200–315 μm) were introduced into a quartz reactor and covered by inactive glass beads. The reactor was positioned in the centre of a hollow stainless-steel cylinder heated by four cartridge heaters inserted around the central hole.

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The reaction temperature was measured with a thermocouple positioned inside the catalytic bed. The catalytic oxidation of propene was conducted at 300 °C for 6 h under a flow of 30 mL min⁻¹ with a gaseous mixture of 20 vol.% O₂ (Praxair 4.5), 10 vol.% C₃H₆ (Praxair 4.6) and 70 vol.% He (Praxair 4.6), the total flow being set at 30 mL min⁻¹. The gaseous products were analyzed every 138 s by an Interscience compact gas chromatograph equipped with an Rtx-1, 1.5 μm column (15 m × 0.32 mm) followed by an FID, a Poraplot Q (2 m × 0.32 mm) and a Molsieves 5 Å column (5 m × 0.32 mm) followed by a TCD and two Poraplot Q columns (2 m and 8 m × 0.32 mm) followed by a second TCD. Acrolein, acetaldehyde, CO and CO₂ were the main products detected. Other compounds (i.e. acetic acid, propene oxide, acetone and acrylic acid) were also detected but only in traces and were thus not considered. Catalytic activity is reported here in terms of conversion of C₃H₆ (number of mol of propene converted per 100 mol of propene introduced) and selectivities [S(C₃H₄O), S(CH₃CHO), S(CO/CO₂) number of mol of acrolein, acetaldehyde, and CO/CO₂ produced per 100 mol of propene converted; in the case of CO/CO₂ and CH₃CHO a factor of 3 and 1.5, respectively, was taken into account]. Gaseous products were also analyzed, every 138 s, by mass spectrometry (ThermoStar Pfeiffer). The principal molecules (H₂O, NH₃, NO, NO₂, N₂) were also detected. The absence or low level of conversion on the supported catalysts was confirmed in the gas phase reactions as above.

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