Direct aerobic epoxidation of alkenes catalyzed by metal nanoparticles stabilized by the H₅PV₂Mo₁₀O₄₀ polyoxometalate†

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Ag and Ru nanoparticles stabilized by H₅PV₂Mo₁₀O₄₀, prepared by a sequence of redox reactions and supported on α-alumina, were effective catalysts for the direct aerobic epoxidation of alkenes in the liquid phase.

The selective aerobic epoxidation of alkenes with molecular oxygen alone remains a key and largely unsolved research objective with significant commercial implications. Apparently, the major obstacle to selective direct aerobic epoxidation of alkenes is the relatively low bond strengths of allylic C–H moieties; facile allylic C–H bond scission commonly leads to (very) low epoxidation selectivity. Thus, the use of heterogeneous silver catalysts, well known for direct aerobic epoxidation of ethylene,¹ can only be extended to substrates that do not have allylic C–H bonds.² Application of molecular oxygen for alkene epoxidation is therefore largely limited to its use in reduced forms such as acylperoxides and peracids,³ alkylhydroperoxides⁴ and hydrogen peroxide,⁵ or in combination with a sacrificial reducing agent, prominently an aldehyde⁶ or hydrogen.⁷ The direct application of molecular oxygen for alkene epoxidation has been reported using ruthenium porphyrin catalysts.⁸ Despite excellent selectivity, the reaction rates apparently are too low for synthetically reasonable application.

We are interested in development of novel strategies for aerobic alkene epoxidation. In this context, it has been observed in the past that (i) certain polyoxometalates, e.g. H₅PV₂Mo₁₀O₄₀, tend to inhibit free radical autooxidation reactions to a certain degree;⁹ in some cases C–H homolytic bond cleavage of hydrocarbons may be inhibited by polyoxometalates. (ii) Polyoxometalates are useful for the stabilization of nanoparticles because their high anionic charge prevents particle aggregation by electrostatic repulsion.¹⁰ Therefore, we hypothesized that nanoparticles stabilized by a polyoxometalate might be effective and more selective catalysts for liquid phase, aerobic alkene epoxidation. Thus, in this paper we describe (i) the preparation of silver and noble metal nanoparticles stabilized by the H₅PV₂Mo₁₀O₄₀ polyoxometalate and then (ii) the use of such metal nanoparticles stabilized by H₅PV₂Mo₁₀O₄₀ and then supported on α-alumina as selective aerobic epoxidation catalysts.

Previously, metal nanoparticles stabilized by polyoxometalates have been prepared in a controlled manner by basically two methods. (i) By reduction, e.g. with hydrogen, of organometallic–polyoxometalate hybrid compounds¹⁰a,b or (ii) by a photoredox reaction of a polyoxometalate with an alcohol to yield a reduced polyoxometalate followed by an additional redox reaction between an added metal cation and the reduced polyoxometalate.¹⁰b For our purposes, these methods had two limitations. First, they were based on the use of polyoxometalates with organic quaternary ammonium cations. Since we are interested in oxidation reactions at relatively high temperatures we wanted to avoid the presence of these organic cations in the catalyst. Second, they were developed for polyoxotungstates that from our experience were much less effective in preventing autooxidation than polyoxomolybdates.⁹c,¹¹

Thus, we sought a novel preparative method that would be applicable for polyoxomolybdates, specifically, H₅PV₂Mo₁₀O₄₀, and that would not require the presence of quaternary ammonium cations. The method developed was based on coupling two redox reactions as presented in Scheme 1. A two-electron reduction of H₅PV₂Mo₁₀O₄₀ with zinc powder was carried out to yield ZnH₅PV₂Mo₁₀O₄₀. This was followed by re-oxidation of the reduced polyoxometalate with the desired metal cation (M = Ag, Ru, Rh, Ir, Pt) to yield the metal nanoparticles stabilized by the polyoxometalate (ZnH₅PV₂Mo₁₀O₄₀ = POM).‡

The nanoparticles of Ag, Ru, Rh, Ir and Pt stabilized by H₅PV₂Mo₁₀O₄₀ were analyzed by transmission electron microscopy. For a representative example, Agₓ-POM deposited from solution, shown in Fig. 1, one can clearly observe the high-contrast silver nanoparticles dispersed in a “sea” of the polyoxometalate.

Average particle sizes for the various Mₓ-POM systems ranged from 2.6 nm for Ptₓ-POM to ~5 nm for Agₓ-POM and Ruₓ-POM with an approximate size dispersion of about ± 25%. The more exact particle sizes and the particle size distributions of some samples were obtained by manual counting on a data set of about 250 nanoparticles. Fig. 2.

\[
\begin{align*}
\text{H}_5\text{PV}^{\text{V}}\text{2Mo}_{10}\text{O}_{40} + \text{Zn} & \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{ZnH}_5\text{PV}^{\text{V}}\text{2Mo}_{10}\text{O}_{40} \quad \text{(blue)} \\
\text{ZnH}_5\text{PV}^{\text{V}}\text{2Mo}_{10}\text{O}_{40} + \text{M}^{\text{II}} & \quad \xrightarrow{\text{M}^{\text{II}}} \quad \text{M}^{\text{II}}-\text{ZnH}_5\text{PV}^{\text{V}}\text{2Mo}_{10}\text{O}_{40}
\end{align*}
\]

Scheme 1 Redox reaction sequence for the preparation of metal nanoparticles stabilized by POM.§

† Electronic supplementary information (ESI) available: Full experimental details. See http://dx.doi.org/10.1039/b507411h

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Further EDS measurements on the deposited samples gave a reasonable confirmation of the amounts of metallic nanoparticles and polyoxometalate as indicated from the reaction stoichiometry, Scheme 1. In other words averaged over an area of 1 μm² there was a ratio of Ag : Zn : P : V : Mo = 2.2 : 1.0 : 1.1 : 2.1 : 10 (experimental) compared to 2 : 1 : 1 : 2 : 10 (theoretical) for Ag₅–Zn₄H₃PV₂Mo₁₀O₄₀. A ratio of Ru : Zn : P : V : Mo = 1.3 : 0.9 : 1.2 : 2.1 : 10 (experimental) compared to 1 : 1 : 1 : 2 : 10 (theoretical) for Ru₅–Zn₄H₃PV₂Mo₁₀O₄₀, and a ratio of Pt : Zn : P : V : Mo = 1.0 : 0.9 : 1.1 : 2.1 : 10 (experimental) compared to 1 : 1 : 1 : 2 : 10 (theoretical) for Pt₅–Zn₄H₃PV₂Mo₁₀O₄₀. For the catalytic reactions described below it was observed that supported catalysts gave the best performance for the aerobic epoxidation of olefins. Various supports were tested including high surface area γ-alumina and silica, and low surface area α-alumina. The Mn–POM nanoparticles were supported by wet impregnation. Only for silica, and low surface area α-alumina supports were tested including high surface area γ-alumina. From the combined results presented in Schemes 2 and 3, Table 1 and Fig. 4 the following observations and conclusions can be drawn.

The results as shown in Schemes 2 and 3 represent relatively very high yields of epoxidation products, which indicates that indeed the use of metal nanoparticles stabilized by H₃PV₂Mo₁₀O₄₀ can catalyze an aerobic epoxidation through inhibition of the formation of allylic oxidation products through autooxidation reactions. There are, however, considerable amounts of non-detected products, probably polymeric oxygenated products; therefore the mass balance is limited. The results gave the impetus for further investigation of the catalytic activity towards epoxidation of more alkenes. Table 1.

The results showed that after short reaction times significantly high epoxide selectivity was obtained, with the caveat that with lower boiling point alkene substrates, reactivity was reduced, presumably due to limited solubility of the alkene in the liquid phase at the reaction temperature. Especially noticeable was the high reactivity of cyclododecene. The catalytic activity was further analyzed by carrying out reaction to high(er) conversions using 1-oc tene as a model substrate, Fig. 4. From this figure one may observe that although initially the reaction selectivity towards formation of the 1-oc tene oxide was very high as the reaction progressed the selectivity decreased via formation of non-detected products (by GC and GC-MS).

From the combined results presented in Schemes 2 and 3, Table 1 and Fig. 4 the following observations and conclusions can be drawn.

### Table 1 Epoxidation of alkenes catalyzed by Mn₅–POM/γ-Al₂O₃ (M = Ru, Ag)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Epoxide yield</th>
<th>Mass balance</th>
<th>Epoxide yield</th>
<th>Mass balance</th>
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</thead>
<tbody>
<tr>
<td>1-Dodecene</td>
<td>23</td>
<td>92</td>
<td>24</td>
<td>79</td>
</tr>
<tr>
<td>1-Decene</td>
<td>20</td>
<td>90</td>
<td>23</td>
<td>82</td>
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<td>1-Octene</td>
<td>15</td>
<td>93</td>
<td>18</td>
<td>88</td>
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<td>1-Heptene</td>
<td>2</td>
<td>100</td>
<td>5</td>
<td>86</td>
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<tr>
<td>1-Hexene</td>
<td>0</td>
<td>—</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>2-Methyl-1-heptene</td>
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<td>100</td>
<td>5</td>
<td>100</td>
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<td>2-Octene</td>
<td>19</td>
<td>100</td>
<td>18</td>
<td>80</td>
</tr>
<tr>
<td>Cyclododecene</td>
<td>24</td>
<td>70</td>
<td>36</td>
<td>47</td>
</tr>
</tbody>
</table>

### Scheme 2 Aerobic epoxidation of cyclohexene catalyzed by Mn₅–POM (M = Ag, Ru).

Table 1 and Fig. 4 the following observations and conclusions can be drawn.
be made: (i) Most importantly, at the beginning of the reaction, epoxides were formed very effectively with little co-formation of additional products, for example a ~25% yield for 1-octene oxide with >90% mass balance, a ~60% yield for cyclooctene oxide at ~100% mass balance, and 40–50% yield for cyclohexene oxide at a 40–50% mass balance. (ii) There is a tendency that as the conversion increased (especially noticeable for less reactive terminal alkenes), the selectivity of the epoxidation reaction decreased to approximately ~50%. There was no significant change in selectivity upon carrying out the reaction at a higher temperature (190 °C) or lower temperature (150 °C). (iii) There was a noticeable induction period for reactions catalyzed by Ag$_n$–POM/α-Al$_2$O$_3$. (iv) POM/α-Al$_2$O$_3$ and Pt$_n$–POM/α-Al$_2$O$_3$ (results not shown) were inactive for alkene epoxidation. (v) The reduced, i.e. less than 100%, mass balance was due to formation of polymeric by-products.** (vi) Control experiments 1-octene/solvent and 1-octene/α-Al$_2$O$_3$/solvent showed no reaction after 1 h and 35–40% reaction with ~35% epoxide selectivity after 4 h. This is in line with typical thermal autoxidation profiles in the absence of metal catalysts.**(vii) α-Al$_2$O$_3$ impregnated with AgNO$_3$, RuCl$_3$, Ag$_n$ and Ru$_n$ showed the formation of allylic oxidation products and reaction profiles similar to those involving 1-octene/α-Al$_2$O$_3$/solvent. (viii) IR spectra after the reaction did not show the typical absorption peaks of the polyoxometalate and therefore indicated the decomposition (no polyoxometalate was found in solution) of the polyoxometalate species on the alumina surface. Thus, also a recycled catalyst did not show the same activity/selectivity as a pristine sample.

Importantly, one can therefore conclude that it would appear that both the Ru$_n$–POM/α-Al$_2$O$_3$ and Ag$_n$–POM/α-Al$_2$O$_3$ catalysts were capable of catalyzing the direct epoxidation of alkenes with oxygen in the liquid phase. The decrease in epoxide selectivity over time was apparently due to competing autoxidation, which is inhibited for only a limited period of time. This may be related to the loss of the polyoxometalate structure during the reaction. Notably, however, addition of more H$_2$PV$_2$Mo$_7$O$_{24}$O$_{10}$ to the catalysts did not ameliorate the situation. At this time, it would still be very presumptuous to give a mechanistic explanation for the initial high selectivity obtained in these direct epoxidation reactions. Given the high initial selectivity for epoxidation of alkenes, the next stage of the research will be to carry out the reactions in the gas phase.

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### Notes and references

† In a typical procedure, 10 mM H$_2$PV$_2$Mo$_7$O$_{24}$O$_{10}$ in water was treated with an excess of zinc powder under argon. An excess of Zn$^2+$ was used to ensure complete reduction of the polyoxometalate. After the color of the solution turned blue indicating formation of [PV$_2$Mo$_7$O$_{24}$O$_{10}$]$^5−$, the solution was filtered to remove the remaining Zn$^2+$ and the filtrate was diluted to 1 mM.

The solution of the reduced polyoxometalate was treated under sonication with the appropriate amount of metal salt (see the experimental section for full details). After 10 min the color turned yellow, indicating the re-oxidation of the polyoxometalate and the formation of metallic nanoparticles. The solutions remained clear to the eye. § The identity of the specific counterions on the polyoxometalate cannot be determined absolutely in solution. However, since eventually the catalyst is supported on a matrix and the elemental analysis by EDS indicated that one equivalent of zinc was indeed needed to reduce the polyoxometalate, we use the formulation as indicated in Scheme 1 although it is clear that Zn$^{2+}$ cations may exchange with H$^+$ cations in the solution.

¶ Reaction conditions: 0.5 mmol cyclohexene, 15 mg (5% w/w) Mn–POM/α-Al$_2$O$_3$, 0.05 mmol anisole (internal standard), 0.5 mL trifluoromethylbenzene (solvent), 2 atm O$_2$, 160 °C, 1 h. The non-detected products were quantified by % missing compound relative to anisole. Anisole was shown to be nonreactive both in situ and separately. Its use as external standard gave statistically identical results.

¶ Reaction conditions: 0.5 mmol 1-methylocyclohexene, 15 mg (5% w/w) Mn–POM/α-Al$_2$O$_3$, 0.05 mmol anisole (internal standard), 0.5 mL trifluoromethylbenzene (solvent), 2 atm O$_2$, 160 °C, 1 h. The reaction with Mn–POM/α-Al$_2$O$_3$ was carried out at 125 °C. The non-detected products were quantified by % missing compound relative to anisole. ** Alkenes did not react under anaerobic conditions and oxides (cyclooctene oxide, 1-octene oxide) were stable under reaction conditions. Also a reaction workup involving filtration of the catalysts, evaporation of the volatile reaction components (substrate, detected products and solvent) followed by dissolution of the remainder in deuterated DMSO yielded an 1H NMR spectrum with peaks in the area of 3–4 ppm indicative of reaction products were quantified by % missing compound relative to anisole.

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