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Direct aerobic epoxidation of alkenes catalyzed by metal nanoparticles stabilized by the $H_5PV_2Mo_{10}O_{40}$ polyoxometalate†

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Received (in Cambridge, UK) 26th May 2005, Accepted 2nd August 2005
First published as an Advance Article on the web 19th August 2005
DOI: 10.1039/b507411h

Ag and Ru nanoparticles stabilized by $H_5PV_2Mo_{10}O_{40}$, 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] alkylhydroperoxides[4] and hydrogen peroxide,[5] or in combination with a sacrificial reducing agent, prominently an aldehyde[6] 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.* $H_5PV_2Mo_{10}O_{40}$, 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 $H_5PV_2Mo_{10}O_{40}$ polyoxometalate and then (ii) the use of such metal nanoparticles stabilized by $H_5PV_2Mo_{10}O_{40}$ 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 compounds[10a,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.[10c] 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 autoxidation than polyoxomolybdates.[9c,11]

Thus, we sought a novel preparative method that would be applicable for polyoxomolybdates, specifically, $H_5PV_2Mo_{10}O_{40}$, 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 $H_5PV^V{}_2Mo_{10}O_{40}$ with zinc powder was carried out to yield $ZnH_5PV^{IV}{}_2Mo_{10}O_{40}$. 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 ($ZnH_3PV_2Mo_{10}O_{40}$ = POM).‡

The nanoparticles of Ag, Ru, Rh, Ir and Pt stabilized by $H_5PV_2Mo_{10}O_{40}$ were analyzed by transmission electron microscopy. For a representative example, Ag_n-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 M_n–POM systems ranged from 2.6 nm for Pt_n-POM to ~5 nm for Ag_n-POM and Ru_n-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.

$$\underset{\text{(orange)}}{H_5PV^V{}_2Mo_{10}O_{40}} + Zn \xrightarrow{H_2O} \underset{\text{(blue)}}{ZnH_5PV^{IV}{}_2Mo_{10}O_{40}}$$

$$ZnH_5PV^{IV}{}_2Mo_{10}O_{40} + M^{n+} \longrightarrow M^0\text{–}ZnH_3PV^V{}_2Mo_{10}O_{40}$$

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

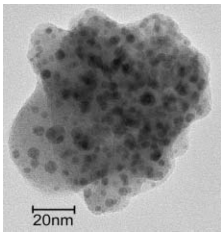

Fig. 1 Transmission electron micrograph for Ag_n-POM deposited from solution.

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

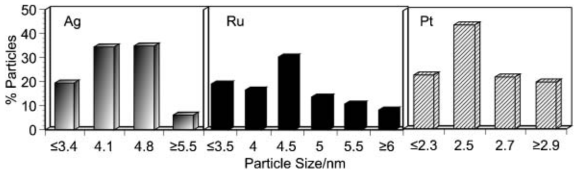


Fig. 2 Particle size distribution for M_n–POM (M = Ag, Ru, Pt). There were essentially no particles outside the given values.

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 μm^2 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 Ag_n–$ZnH_3PV_2Mo_{10}O_{40}$, 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 Ru_n–$ZnH_3PV_2Mo_{10}O_{40}$, 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 Pt_n–$ZnH_3PV_2Mo_{10}O_{40}$. 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 are γ-alumina and silica, and low surface area α-alumina. The M_n–POM nanoparticles were supported by wet impregnation. Only for α-alumina were homogeneously well-dispersed M_n–POM nanoparticles obtained. Presumably, despite the high surface area the small pore size of γ-alumina and silica, compared to the nanoparticle size, prevented their effective adsorption onto the matrix surface. IR measurements confirmed that after impregnation the "Keggin" structure of the polyoxometalate remained intact (peaks at 1080, 962, 868 and 796 cm^{-1}). Transmission electron micrographs of M_n–POM on α-alumina are shown in Fig. 3. In these images, one can clearly observe the metal nanoparticles sampled near thin edges of the α-alumina. In other areas the alumina matrix was too thick for meaningful interpretation.

Direct aerobic epoxidation of alkenes catalyzed by the various M_n–POM nanoparticles supported on α-Al_2O_3 was first carried out on substrates such as cyclohexene and 1-methylcyclohexene known to be highly sensitive to autooxidation with significant formation of allylic oxidation products; for these substrates epoxidation with oxygen is not preferred.[12] In Schemes 2 and 3 are presented the results of the aerobic epoxidation reaction for two cyclohexene derivatives.

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 $H_5PV_2Mo_{10}O_{40}$ 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.

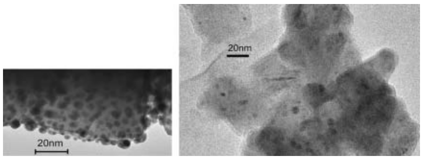
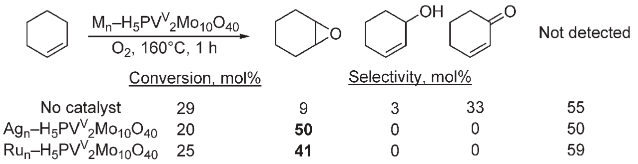
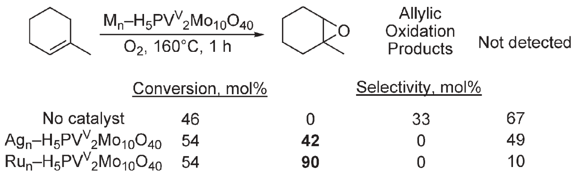


Fig. 3 TEM image for Ag_n–POM (left) and Ru_n–POM (right) nanoparticles on the edge of a α-alumina matrix.



	Conversion, mol%	Selectivity, mol%			
No catalyst	29	9	3	33	55
Ag_n–$H_5PV^V_2Mo_{10}O_{40}$	20	**50**	0	0	50
Ru_n–$H_5PV^V_2Mo_{10}O_{40}$	25	**41**	0	0	59

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



	Conversion, mol%	Selectivity, mol%		
No catalyst	46	0	33	67
Ag_n–$H_5PV^V_2Mo_{10}O_{40}$	54	**42**	0	49
Ru_n–$H_5PV^V_2Mo_{10}O_{40}$	54	**90**	0	10

Scheme 3 Aerobic epoxidation of 1-methylcyclohexene catalyzed by M_n–POM (M = Ag, Ru).||

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-octene as a model substrate, Fig. 4. From this figure one may observe that although initially the reaction selectivity towards formation of the 1-octene 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

Table 1 Epoxidation of alkenes catalyzed by M_n–POM/α-Al_2O_3 (M = Ru, Ag)

	Ru_n–POM/α-Al_2O_3		Ag_n–POM/α-Al_2O_3	
Substrate	Epoxide yield[a]	Mass balance[a]	Epoxide yield[a]	Mass balance[a]
1-Dodecene	23	92	24	79
1-Decene	20	90	23	82
1-Octene	15	93	18	88
1-Heptene	2	100	5	86
1-Hexene	0	—	0	—
2-Methyl-1-heptene	15	100	5	100
2-Octene	19	100	18	80
2-Methyl-2-heptene[b]	24	70	36	47
Cyclododecene[c]	60	100	66	100

[a] The epoxide yield was measured as the amount of epoxide formed using anisole as the standard and the mass balance is a measure of the amount of detected product and remaining substrate. No other products beside epoxide were detected in the GC and GC analyses. [b] 130 °C. [c] A ~50/50 mixture of *trans*/*cis* isomers gave a 80/20 ratio of *trans*/*cis* epoxide by GC analysis. [d] Reaction conditions: 0.5 mmol 1-alkene, 15 mg (5% w/w) M_n–POM/α-Al_2O_3, 0.05 mmol anisole, 0.5 mL trifluoromethylbenzene, 2 atm O_2, 170 °C, 30 min (Ru), 1 h (Ag).

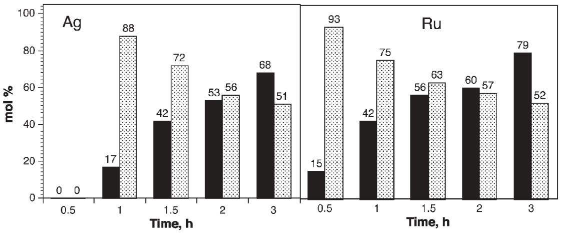


Fig. 4 Aerobic epoxidation of 1-octene by M–POM/α-Al_2O_3 (black bars–conversion (mol% 1-octene reacted), grey bars–mass balance (mol% 1-octene oxide/mol % all products-1-octene and non-detected)).

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 cyclododecene 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_2O_3. (iv) POM/α-Al_2O_3 and Pt_n–POM/α-Al_2O_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_2O_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 autooxidation profiles in the absence of metal catalysts.[13] (vii) α-Al_2O_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_2O_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_2O_3 and Ag_n–POM/α-Al_2O_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 autooxidation, 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 $H_5PV_2Mo_{10}O_{40}$ 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.

The research was supported by the Israel Science Foundation (Grant No. 315/03), the Minerva Foundation, and the Kimmel Center for Molecular Design. R.N. is the Rebecca and Israel Sieff Professor of Organic Chemistry.

Notes and references

‡ In a typical procedure, 10 mM $H_5PV_2Mo_{10}O_{40}$ in water was treated with an excess of zinc powder under argon. An excess of Zn^0 was used to ensure complete reduction of the polyoxometalate. After the color of the solution turned blue indicating formation of $[PV^{IV}{}_2Mo_{10}O_{40}]^{7-}$ the solution was filtered to remove the remaining Zn^0 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 counteractions 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) M_n–POM/α-Al_2O_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-methylcyclohexene, 15 mg (5% w/w) M_n–POM/α-Al_2O_3, 0.05 mmol anisole (internal standard), 0.5 mL trifluoromethylbenzene (solvent), 2 atm O_2, 160 °C, 1 h. The reaction with Ru_n–POM/α-Al_2O_3 was carried out at 130 °C. The non-detected products were quantified by % missing compound relative to anisole.

** Alkenes did not react under anaerobic conditions and oxides (cyclohexene 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 oxygenated compounds as non-volatile products. These remaining compound(s) could not be eluted under any GC/MS conditions; likely they are polymers. The mass of these remaining compound(s) is in accordance with the computed mass balance.

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