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Stabilization of Palladium Nanoparticles by Polyoxometalates Appended with Alkylthiol Tethers and their Use as Binary Catalysts for Liquid Phase Aerobic Oxydehydrogenation

Mario De bruyn[a] and Ronny Neumann[a,*]

[a] Department of Organic Chemistry, Weizmann Institute of Science, Rehovot, Israel 76100
Fax: +972-8-934-3354; e-mail: Ronny.Neumann@weizmann.ac.il

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Abstract: A polyoxometalate with two alkyl thiol appendages, $Q_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2SH)_2]$ (Q = ammonium salt) stabilized the formation of palladium nanoparticles. This tethered polyoxometalate–palladium binary catalyst was effective for the aerobic oxydehydrogenation of vinylcyclohexene and vinylcyclohexane to styrene as the major product *via* activation of the allylic, tertiary carbon-hydrogen bond.

Keywords: dehydrogenation; homogeneous catalysis; oxidation; oxygen; palladium; polyoxometalates

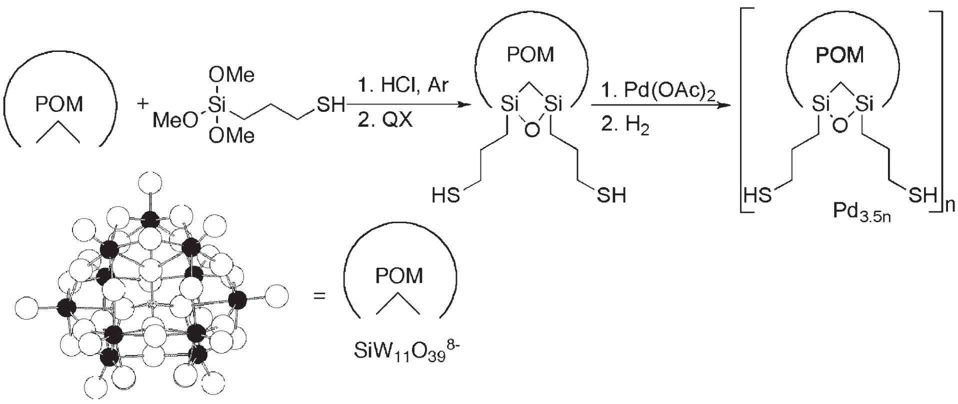
Catalysis by metallic nanocrystals, colloids or nanoparticles is a well-established field that has undergone a renaissance with the realization that classically observed reactivity and/or selectivity may be significantly modified by various means such as control of particle size, metal-metal interactions within particles, and particle-support interactions. A non-inclusive list of a few, notable examples includes the size-dependent adsorption of CO on gold crystals,[1] the advantage of using gold with palladium for the aerobic oxidation of alcohols,[2] and the use of gold on silica supports for epoxidation of propene with H_2/O_2.[3] Polyoxometalates are also an interesting class of compounds with much structural variability,[4] which have received increasing attention as oxidation catalysts because of their various advantageous properties including intrinsic stability and electron-acceptor properties.[5] Until recently most applications of polyoxometalates have been oriented to their use as stand-alone oxidation catalysts. There are now observations that polyoxometalates may stabilize high-valent oxidation states of previously unobserved noble metal oxo species[6] and they can lead to oxidation of pendant metal-organic centers.[7] Also, by virtue of their high anionic charge, polyoxometalates can be used to stabilize nanoparticles.[8] These properties have led to new binary catalytic systems. We have reported that a platinum(II) bipyridinium-polyoxometalate binary complex is effective for the aerobic oxidation of methane[9] and nanoparticles stabilized by polyoxometalates lead to improved catalytic activity in carbon-carbon coupling reactions,[10] and improved selectivity in aerobic alkene epoxidation reactions.[11]

Palladium nanoparticles have often been used in catalytic applications;[12] their stabilization with alkylthiols is less commonly used,[13] because of the ingrained perception that alkylthiols and thiolates are poisons that inhibit catalysis.[14] In this paper we present a significant extension of the use of polyoxometalate binary catalytic systems wherein a polyoxometalate appended with alkylthiol tethers is used to complex a palladium(II) center. Upon reduction with hydrogen, nanoparticles are formed that are stabilized by the polyoxometalate appended with the alkylthiol tethers. This catalytic system shows uniquely and largely unexpected high activity and significantly improved selectivity for aerobic oxydehydrogenation of vinylcyclohexene and vinylcyclohexene to styrene.

The binary catalyst was obtained by first reacting trimethoxymercaptopropylsilane, $(MeO)_3SiCH_2CH_2CH_2SH$, with a lacunary polyoxometalate, $[SiW_{11}O_{39}]^{8-}$, to obtain $Q_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2SH)_2]$ with $Q = (C_4H_9)_4N^+$, $(C_6H_{13})_4N^+$, and Aliquat®, i.e., predominantly $(C_8H_{17})_3CH_3N^+$, *via* a modified literature procedure (Scheme 1).[15]

Palladium nanoparticles stabilized by $Q_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2SH)_2]$ were obtained by adding $Pd(OAc)_2$ (optimally *ca.* 3.6 equivalents; see also below) to a solution of $Q_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2SH)_2]$ followed by reduction with H_2. A typical transmission electron micrograph (Figure 1) shows the formation of small Pd nanocrystals of 2–6 nm whose size distribution depended somewhat on the quaternary ammonium counter cation, but consisted mainly of particles of 4–5 nm.

Importantly the electron diffraction pattern [Figure 1 (insert)] clearly indicates the formation of palladium crystallites; the tethered polyoxometalates



Scheme 1. Outline of the synthetic procedure for the preparation of the palladium–polyoxometalate binary catalyst.

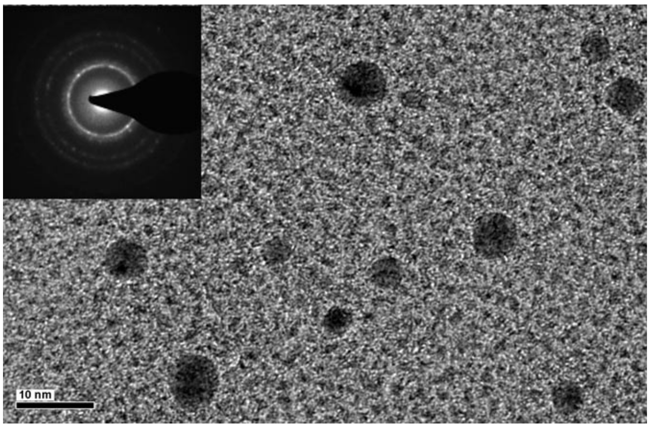
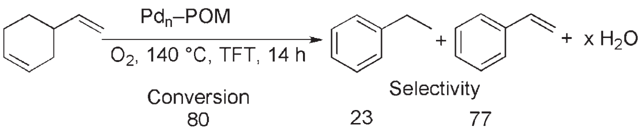


Figure 1. Transmission electron micrograph of Pd crystals stabilized by $[(C_6H_{13})_4N]_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2SH)_2]$ with the electron diffraction pattern shown as an insert.

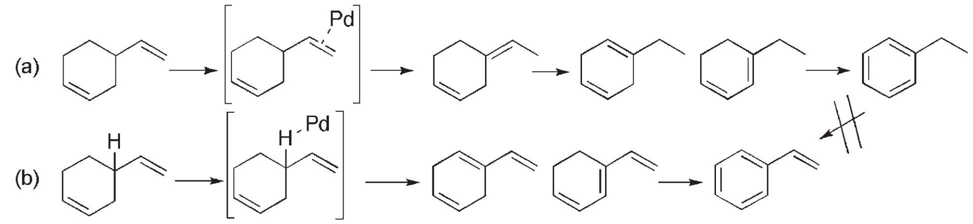
are dispersed throughout. It should also be stressed that it was not possible to stabilize palladium nanoparticles in this manner by the non-functionalized lacunary polyoxometalate ($Q_5H_3SiW_{11}O_{39}$) alone or with a polyoxometalate appended by non-reactive appendages such as chloroalkyl tethers, $Q_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2Cl)_2]$. Upon reduction of the $Pd(OAc)_2$ in the presence of either $Q_5H_3SiW_{11}O_{39}$ or $Q_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2Cl)_2]$, palladium black or mirrors were obtained.



Scheme 2. Results for the aerobic oxydehydrogenation of 4-vinylcyclohexene catalyzed by Pd_n-POM.

Dehydrogenation and oxydehydrogenation have significant commercial potential for oxidation of alkanes to alkenes, and alkylarenes to vinylarenes.[16] In this context we have first investigated the suitability of the palladium–polyoxometalate binary catalyst for the oxydehydrogenation of 4-vinylcyclohexene to styrene. This transformation could prove to be important because 4-vinylcyclohexene is easily accessible from 1,3-butadiene and the oxydehydrogenation would provide a different pathway to styrene. Under *optimized* experimental conditions, the palladium–polyoxometalate binary catalyst {Pd_n-POM, *ca.* 25 μmol Pd, POM = $[(C_6H_{13})_4N]_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2SH)_2]$} dispersed in solution catalyzed the oxydehydrogenation of 4-vinylcyclohexene (1 mmol) under 4 bar O_2 at 140 °C for 14 h in α,α,α-trifluorotoluene (TFT, 4 mL) to yield styrene and ethylbenzene as the only products (Scheme 2).

The results show high conversions with notably high selectivity to the more dehydrogenated and desired styrene product.[17] Control and comparative oxydehydrogenation reactions under the same conditions revealed the following: (i) Direct use of $Pd(OAc)_2$ also showed initial formation of styrene, but aggregated quickly to palladium black/mirror, which was coupled to reaction inhibition. Also a large number of oxygenated by-products were formed. (ii) $Q_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2SH)_2]$ alone was not catalytically active.[18] (iii) The optimum Pd/POM ratio was about 3.6; lower ratios gave less selectivity to styrene at similar conversions, whereas at higher ratios the nanoparticles were unstable. (iv) At 0.2 and 2 atm O_2 the conversions were 42% and 70%, respectively, with lower selectivity to styrene, 3% and 45%, respectively. Higher O_2 pressures were not studied due to safety limitations. (v) Pd_n-POM supported by wet impregnation on matrices such as α-alumina, γ-alumina and titanium oxide showed similar reaction conversions, but lower selectivity to styrene of 50–60% only slightly depending on the support used. (vi) Other aromatic solvents such as benzene and fluorobenzene can also be used as solvent with some improvement in the selectivity to styrene but at the expense of reduced conversion. For example, a reaction in benzene



Scheme 3. Pathways for the formation of ethylbenzene and styrene.

yielded a styrene/ethylbenzene ratio of 82/18 but at only 37% conversion. Alkylated aromatics such as toluene and xylene showed some autooxidation of the solvent. (vii) Similar oxydehydrogenation of phenylcyclohexene yielded biphenyl (84% conversion, *ca.* 95% selectivity). (viii) Reaction profiles showed that the reaction was closely first order in the 4-vinylcyclohexene substrate with no significant accumulation of intermediates, such as other dienes by isomerization or oxygenated products. A constant styrene/ethylbenzene ratio was observed also indicating that ethylbenzene was not an intermediate to the formation of styrene. (ix) Indeed, an independently attempted oxidation of ethylbenzene was not successful. (x) It should be also noted that the Pd_n-POM catalysts appear to be stable to the reaction conditions, no aggregation of palladium and formation of palladium black were observed. Direct TEM measurements were not possible because of the presence of organic residues. The combined results underline the positive effect of the alkylthiol tethered polyoxometalate on the stabilization of Pd(0) in solution and the ability of this binary system to catalyze oxydehydrogenation.

The high selectivity to styrene and the fact that ethylbenzene once formed did not further react raises interesting mechanistic questions concerning this reaction. Thus, it is logical to conclude that ethylbenzene and styrene are formed by different reaction pathways as hypothesized in Scheme 3. Therefore, isomerization of the exocyclic double bond, reasonably through interaction of Pd with the π-electrons of the double bond followed by thermodynamically favored aromatization of the endocyclic diene, will lead to ethylbenzene (pathway a) whereas oxydehydrogenation first *via* activation of the reactive tertiary carbon-hydrogen bond followed by an additional more facile aromatization will lead to styrene (pathway b).

In order to support the above mechanistic conjecture we next used vinylcyclohexane as a probe substrate. This compound did not yield any oxydehydrogenation product in the presence of palladium acetate, forming only a palladium mirror, yet in the presence of Pd_n-POM it did yield oxydehydrogenation products, that is, vinylcyclohexenes, ethylbenzene and styrene according to the reaction profile presented in Figure 2.

From the reaction profile presented, one may observe a fast (within 1 h) dehydrogenation to a mixture of vinylcyclohexenes > styrene > ethylbenzene. The reaction then decelerated and further slower conversion of the starting compound, vinylcylohexane, was competitively accompanied by dehydrogenation of the intermediate vinylcyclohexenes to styrene > ethylbenzene. Importantly, the relative amount of ethylbenzene remains constant, while the ratio of vinylcyclohexenes + styrene/ethylbenzene is *ca.* 3:1, a value similar to the value observed in the oxydehydrogenation of vinylcyclohexene as substrate (Scheme 2).

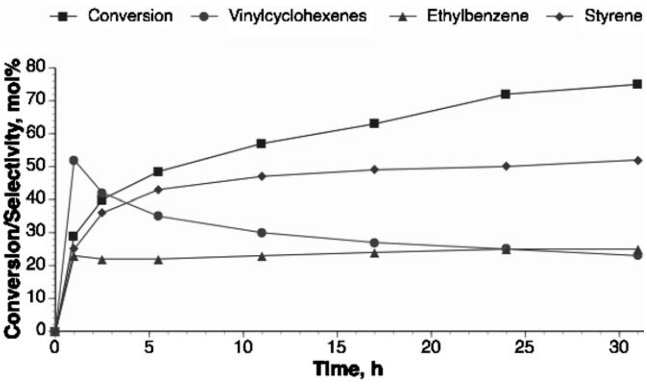


Figure 2. Reaction profile (conversion and product selectivity) for the oxydehydrogenation of vinylcyclohexane.

In conclusion, Pd nanoparticles stabilized by polyoxometalates appended with alkylthiol tethers are effective binary catalysts for aerobic oxydehydrogenation of substrates with reactive allylic tertiary carbon-hydrogen bonds. Apparently, this is the first time that thiol moieties, which generally are thought to deactivate noble metals, have been used in such a beneficial manner. Using such concepts, we are seeking yet more active and selective catalysts for the aerobic oxydehydrogenation of alkanes to alkenes.

Experimental Section

Tethered Salts of 'Keggin' Polyoxometalate, $K_8SiW_{11}O_{39}$

The lacunary 'Keggin' polyoxometalate, $K_8SiW_{11}O_{39}$ was synthesized according to an existing literature procedure.[19] The polyoxometalate was tethered with propylthiol moieties by mixing 10 g $K_8SiW_{11}O_{39}$ dissolved in 2:1 water/acetonitrile mixture at pH 4 (adjusted with HCl) with 2.75 mL trimethoxymercaptopropylsilane dissolved in 4 mL acetonitrile. The pH was adjusted to 1 and the mixture left stirring overnight at room temperature. The acetonitrile was removed from the reaction mixture by evaporation and 12 g tetrabutylammonium bromide were added. The mixture was left stirring for another 2 h, the precipitate was collected and consecutively washed with water, 2-propanol and diethyl ether. The powder was dried under vacuum for several hours. The $(C_6H_{13})_4N^+$ and Aliquat® salts of the tethered polyoxometalate were obtained following a slightly different procedure: here the ammonium salt was added to the reaction medium, after which the acetonitrile was gradually removed. The Aliquat® salt of $Q_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2SH)_2]$ could be filtered immediately while the $(C_6H_{13})_4N^+$ salt of $Q_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2SH)_2]$ required the addition of an excess of 2-propanol. The powders obtained were washed and dried as described above. $Q_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2SH)_2]$, for example $[Q=(C_6H_{13})_4N^+]$ was characterized by ^1H NMR at 400 MHz (DMSO-d_6): $\delta=0.65$ (t, 4H, $SiCH_2$), 0.86 (t, 48H, $CH_2C\mathit{H}_3$), 1.27 (m, 96H, $CH_2CH_2CH_2$), 1.55 (m, 32H, $C\mathit{H}_2CH_2N^+$), 1.73 (m, 4H, $C\mathit{H}_2CH_2SH$), 2.13 (t, 2H, SH), 2.54 (triplet of doublets, 4H, $CH_2C\mathit{H}_2SH$), 3.15 (t, 32H, CH_2N^+); ^{29}Si-NMR (79.495 MHz, ^1H-decoupled, DMSO-d_6): $\delta=-53$ (s, 2Si), -85 (s, 1Si); ^{183}W NMR (16.671 MHz, DMSO-d_6): $\delta=-105$, -107, -111, -126, -172, -251; IR: $\nu=534$ (ν_{sym} WOW), 707 (ν_{asym} WOW), 753 (ν_{asym} WOW), 805 (ν_{asym} WOW), 855 (ν_{asym} WOW), 924 (ν_{asym} W=O), 947 (ν_{asym} W=O), 963 (ν_{asym} W=O), 1044 (ν_{asym} Si-O-Si), 1484 (C-H), 2566 (S-H), 2873 (C-H), 2934 (C-H), 2961 cm^{-1} (C-H); anal. calcd. for $C_{102}H_{222}N_4O_{40}S_2Si_3W_{11}$ (4315.49): (found) C 28.39 (28.58), H 5.19 (5.21), N 1.30 (1.33), Si 1.95 (2.2), W 46.86 (45.0). CHN were measured by pyrolysis and Si, W were measured by EDS.

Palladium Nanoparticles

Palladium nanoparticles were prepared by dissolving 0.0886 mmol $Q_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2SH)_2]$ in TFT (10 mL). After saturation of the solution with H_2, a TFT (10.5 mL) solution of $Pd(OAc)_2$ (55.5 mg) was added attaining a molar $Pd/Q_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2SH)_2]$ ratio of *ca.* 3.6. The solution was kept at 30 °C for 2 h under an H_2 flow. $Q_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2SH)_2]Pd(OAc)_2$ was also observed *in situ* by ^1H NMR by reacting $Q_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2SH)_2]$ with $Pd(OAc)_2$ in DMSO-d_6 for 30 min. The ^1H NMR spectrum of $Q_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2SH)_2]Pd(OAc)_2$ for $Q=(C_6H_{13})_4N^+$ showed peaks at $\delta=0.65$ (t, 4H, $SiCH_2$), 0.86 (t, 48H, $CH_2C\mathit{H}_3$), 1.27 (m, 96H, $CH_2CH_2CH_2$), 1.55 (m, 32H, $C\mathit{H}_2CH_2N^+$), 1.73 (m, 4H, $C\mathit{H}_2CH_2SH$), 2.45 (t, 2H, SH), 2.68 (triplet of doublets, 4H, $CH_2C\mathit{H}_2SH$), 2.80 (s, 6H, $OOCCH_3$), 3.15 (t, 32H, CH_2N^+).

Use of both Aliquat® and tetrahexyammonium counter cation led to well dispersed 4–5 nm particles as presented in Figure 1. In the presence of a tetrabutylammonium cation, the TEM micrograph showed aggregation of similarly sized particles. The aggregation appears to occur during deposition of the sample for the TEM measurement. The use of a tetramethylammonum cation leads to larger ~50 nm particles.

Typical Oxydehydrogenation Procedure

Reactions were carried out in 25-mL glass pressure tubes with Teflon stir bars typically using 1 mmol substrate, 50 μmol Pd as $Pd/Q_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2SH)_2]$ 4 mL α,α,α-trifluorotoluene (TFT), 4 bar O_2, 140 °C. Conversions were calculated with reference to a standard (dodecane). TFT was used as solvent because of its suitable boiling point.

Acknowledgements

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