

Direct Aerobic Oxidation of Secondary Alcohols Catalysed by Pt(0) Nanoparticles Stabilized by $\text{PV}_2\text{Mo}_{10}\text{O}_{40}^{5-}$ Polyoxometalate

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Received: 29 October 2007 / Accepted: 13 December 2007 / Published online: 8 January 2008
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Abstract Pt(0) nanoparticles stabilized by the $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ polyoxometalate were prepared in water by a sequence of redox reactions and supported on α -alumina. Characterization by TEM showed an average particle size of 2.6 nm with an approximate size dispersion of about $\pm 25\%$. EDS analysis confirmed the amounts of metal and polyoxometalate as indicated from the reaction stoichiometry. These nanoparticles were further used as catalysts for the oxidation of secondary alcohols with molecular oxygen to the corresponding carbonyl products. The oxidation of secondary alcohols was further improved by the use of Pt nanoparticles stabilized by $\text{Rh}_{1.7}\text{PV}_2\text{Mo}_{10}\text{O}_{40}$.

Keywords Pt · Nanoparticles · Colloids · Oxidation · Alcohols · Oxygen

1 Introduction

The oxidation of primary and secondary alcohols into the corresponding carbonyl compounds plays an important role in organic synthesis. Therefore, many examples of catalytic processes for this transformation are known [1–3]. Also, there are many examples for the aerobic oxidation of alcohols, including systems that utilize nitroxyl radical such as TEMPO as co-oxidant catalyst [4–6], metal nanoparticles (mostly Pd(0) and Pt(0)) [7–12] and other organo- and inorgano-metallic catalysts [6, 13]. However, these examples often report the aerobic oxidation of activated alcohols such as benzylic and allylic ones, while the

oxidation of secondary alcohols, which are much less activated, and the selective aerobic oxidation of primary alcohols to their corresponding aldehydes, which is very difficult to achieve are rarely reported. Herein we wish to develop strategies for the aerobic oxidation of alcohols. In this context, it has been observed in the past that (i) certain polyoxometalates, e.g. $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$, are good catalysts for the aerobic oxidation of alcohols [2–4, 14] (ii) Polyoxometalates are useful for the stabilization of nanoparticles because their high anionic charge prevents particle aggregation by electrostatic repulsion [15]. Therefore, we hypothesized that the combination between metal nanoparticles and polyoxometalates will produce better catalysts capable of oxidizing non-activated secondary alcohols without any additives. To this aim we developed a system in which metal nanoparticles are stabilized by a polyoxometalate, expecting that it might be more effective for liquid phase, aerobic alcohol oxidation. Thus, in this paper we describe (i) the preparation of platinum nanoparticles stabilized by the $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ and $\text{Rh}_{1.7}\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ polyoxometalates and then (ii) their use, supported on α -alumina, as efficient catalysts for oxidation of alcohols.

2 Experimental

2.1 Preparation of Metal Colloids

Metal colloids were prepared by sonication of metal precursors with reduced $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ [16] or $\text{Rh}_{1.7}\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ solution. The colloids were then supported on α -alumina. $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ or $\text{Rh}_{1.7}\text{PV}_2\text{Mo}_{10}\text{O}_{40}$, 1×10^{-2} M in water solution, was treated with an excess of Zn powder under argon. When the color of the solution

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turned blue, the solution was filtered from the excess of Zn and diluted to 1×10^{-3} M with water.

2.1.1 Pt(0) Colloids Stabilized by $H_5PV_2Mo_{10}O_{40}$

One milliliter of blue $H_5ZnPV_2Mo_{10}O_{40}$ 1×10^{-3} M solution was treated, under sonication, with 0.5 mL K_2 $[PtCl_4]$ solution (0.01 M in H_2O/CH_3CN 1:1). After 10 min, the color turned dark yellow, indicating the re-oxidation of $H_7PV_2Mo_{10}O_{40}$ to $H_5PV_2Mo_{10}O_{40}$ and the formation of Pt (0) nanoparticles (the solution remained clear). TEM analysis showed colloids with an average size of 2.6 nm, EDS analysis showed signals for Pt 18.6%, Mo 73.8%, and V 7.6%. Pt (0) colloids were stirred with α -alumina (5% w/w) for 2 h and then water was removed in high vacuum and dried. The final Pt (0) colloids—on- α -alumina have a gray color and are stable at RT in a dark environment.

2.1.2 Pt(0) Colloids Stabilized by $Rh_{1.7}PV_2Mo_{10}O_{40}$

About 0.9 mL of $H_5PV_2Mo_{10}O_{40}$ 0.01 M solution was mixed with 1.5 mL of $RhCl_3 \cdot 3H_2O$ to get a clear solution of $Rh_{1.7}PV_2Mo_{10}O_{40}$. The solution was further reduced with Zn, filtered and diluted to a concentration of 1×10^{-3} M. One milliliter of blue $Rh_{1.7}ZnPV_2Mo_{10}O_{40}$ 1×10^{-3} M was treated, under sonication, with 0.5 mL K_2 $[PtCl_4]$ solution (0.01 M in H_2O/CH_3CN 1:1). After 10 min, the color turned dark yellow, indicating the re-oxidation of $Rh_{1.7}ZnPV_2Mo_{10}O_{40}$ to $Rh_{1.7}PV_2Mo_{10}O_{40}$ and the formation of Pt (0) nanoparticles (the solution remained clear). TEM analysis showed colloids with an average size of 3.3 nm, EDS analysis showed signals for Pt 7%, Rh 12%, Mo 66%, and V 13%. Pt (0) colloids were stirred with α -alumina (5% w/w) for 2 h and then water was removed in high vacuum and dried. The final Pt (0) colloids—on- α -alumina have a gray color and are stable at RT in a dark environment.

2.2 Oxidation Reactions

All of the alcohols were used without purification, as supplied by Aldrich, Lancaster or Acros. All of the reactions were done in 15 mL pressure tubes and put in an oil bath that was pre-heated to 125 °C. Reactions were run for 14 h, with a 1:20 catalyst/substrate ratio (normally 2.5×10^{-5} mmol catalyst and 5×10^{-4} mmol substrate) or 1:100 catalyst/substrate (normally 5×10^{-6} mmol catalyst and 5×10^{-4} mmol substrate) under 2 bar of O_2 . The liquid products solution were separated from the supported catalyst and analyzed by GC and GC-MS.

2.3 Instrumentation

2.3.1 GLC

Agilent 6890, using a Restek 5MS capillary column (25 m 5% phenylmethyl siloxane with an I.D. of 0.2 mm and 0.33 μ m coating).

2.3.2 GC-MS

HP 5973, using a 30 m 5% phenylmethyl silicone capillary column with an I.D. of 0.32 mm and 0.25 μ m coating (Restek 5MS).

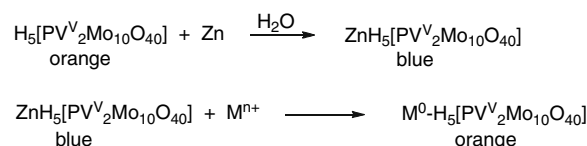
2.3.3 TEM

Philips CM120 Super Twin (120 kV, tungsten/LaB6), Specimen tilt: $\pm 40^\circ$, Holders: single tilt, rotation holder, cryo holder (Gatan 626DH). Accessories: Low dose unit; EDS (energy dispersive spectrometry) for elemental analysis, using retractable Silicon (Li) detector with super ultra thin window (EDAX). Dedicated for material sciences. Point resolution: 3.0 Å.

3 Results and Discussion

Recently, we have reported [17] the preparation of metal nanoparticles stabilized by $H_5PV_2Mo_{10}O_{40}$, by a method we developed that based on coupling two redox reactions as presented in Scheme 1. A two-electron reduction of $H_5PV_2Mo_{10}O_{40}$ with zinc powder was carried out to yield $ZnH_5PV_2Mo_{10}O_{40}$. 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 ($ZnH_3PV_2Mo_{10}O_{40} = POM$).

In this way Pt(0) nanoparticles stabilized by $H_5PV_2Mo_{10}O_{40}$ were prepared and analyzed by transmission electron microscopy (TEM) and EDS. Looking at the image of Pt_n-POM deposited from solution, shown in Fig. 1, one can clearly observe the high-contrast platinum nanoparticles dispersed in a “sea” of the polyoxometalate.



Scheme 1 Redox reaction sequence for the preparation of metal nanoparticles stabilized by polyoxometalate (POM)

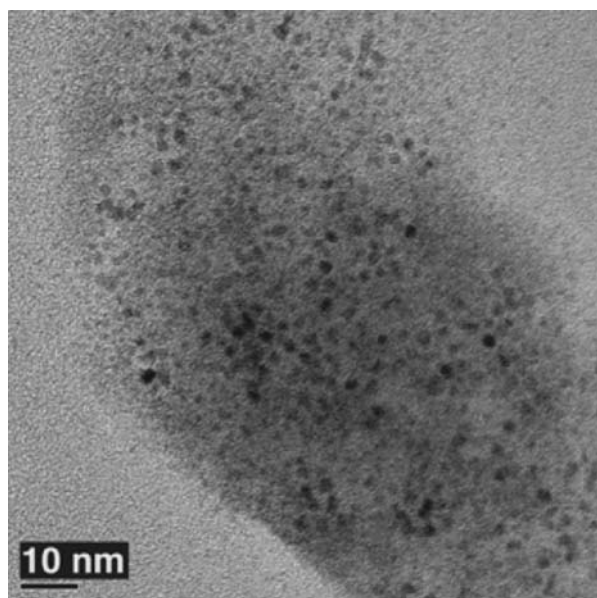


Fig. 1 Transmission electron micrograph for Pt_n -POM deposited from solution

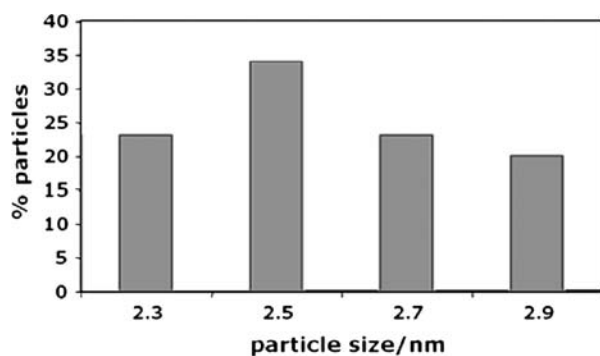


Fig. 2 Particle size distribution for Pt_n -POM

From Fig. 1, one may observe that the particles are homogeneous in size and shape. Indeed, as illustrated in Fig. 2, the particle size distribution is very narrow with an average size of 2.6 nm. 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 $1 \mu\text{m}^2$ there was a ratio of 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 $Pt_n-ZnH_3PV_2Mo_{10}O_{40}$.

3.1 Influence of Different Supports and %Pt on the Catalysis

In order to perform heterogeneous catalysis, colloids were supported on a variety of solid supports (granular α -alumina,

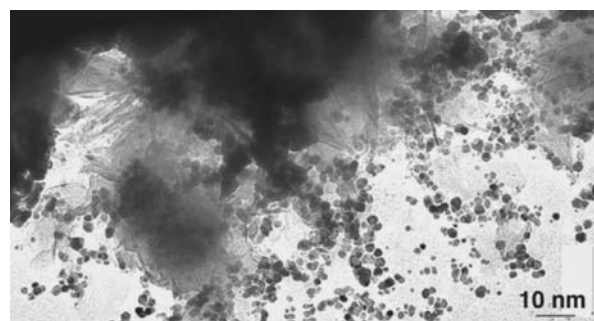


Fig. 3 TEM image of Pt_n -acidic POM supported on α -alumina

powdered α -alumina, γ -alumina, activated coal and hydrophilic silica gel) and tested for their activity in aerobic oxidation of 2-octanol. Different amounts of Pt (0) (1, 5 and 10%) on the support were also tested. The reaction conditions were 0.5 mmol alcohol, 0.005 mmol catalyst, 14 h, 2 bar O_2 , 125 °C. The best results were obtained with 5% Pt_n -POM on α -alumina powder (18% conversion and 2-octanone being the only product). A TEM picture of Pt_n -POM nanoparticles on α -alumina powder is shown in Fig. 3.

3.2 Aerobic Oxidation of Secondary Alcohols by Pt (0) Catalyst

The reaction with 2-octanol was further investigated changing the amount of catalyst and the best yield was achieved at the ratio of 1:20 catalyst: substrate. The catalyst was recycled three times and reactivity of 2-octanol decreased from 70 to 49%. When the catalyst was filtered from the solution the reaction did not proceed even after 5 h, indicating that there is no leaching of the catalyst into the reaction mixture. Using the optimized condition for the oxidation reaction with Pt_n -POM/ α -alumina (1:20 catalyst to substrate ratio, 125 °C, 14 h), aerobic oxidation of additional secondary alcohols was performed yielding ketones as the only products, Table 1.

In attempts to improve the yield of these reactions, the protons of the polyoxometalate $H_5PV_2Mo_{10}O_{40}$ were exchanged by a variety of metal ions to get $M^{+n}_{5/n}PV_2Mo_{10}O_{40}$ [$M = Cu(II), Zn(II), Mn(II), Co(II), Ni(II), Pd(II), Ru(II)$ and $Rh(III)$]. Pt(0) nanoparticles stabilized by these polyoxometalate metal salts were prepared as before, according to Scheme 1, and tested in the oxidation reaction of 2-octanol, showing the best results in the case of $Rh_{12/3}PV_2Mo_{10}O_{40}$. This catalyst was also recycled three times, showing approximately a 30% linear drop in reactivity over the three cycles. The Pt(0) nanoparticles stabilized by $Rh_{12/3}PV_2Mo_{10}O_{40}$ were characterized by TEM showing particles which are homogeneous in size and

Table 1 Aerobic oxidation of secondary alcohols with Pt_n-POM/ α -alumina catalyst

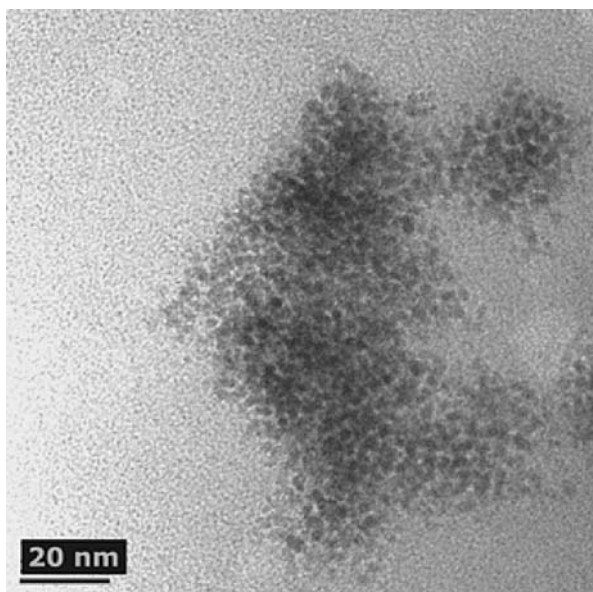
Substrate	Product	Yield (mol%)
2-decanol	2-decanone	50
2-octanol	2-octanone	48
2-hexanol	2-hexanone	54
2-pentanol	2-pentanone	53
Cyclohexanol	cyclohexanone	80
Cyclooctanol	cyclooctanone	95

Conditions: 5×10^{-4} mole alcohol, 2.5×10^{-5} mole catalyst (1:20), 0.5 mL toluene, 125 °C, 14 h, 2 atm. O₂

Table 2 Aerobic oxidation of secondary alcohols with Pt_n-POM/ α -alumina and Pt_n-RhPOM/ α -alumina catalyst

Substrate	TON with Pt _n -POM/ α -alumina	TON with Pt _n -RhPOM/ α -alumina
2-decanol	12	47
2-octanol	14	44
2-hexanol	8	52
2-pentanol	10	51
cyclohexanol	13	67
cyclooctanol	18	87

Conditions: 5×10^{-4} mol alcohol, 5×10^{-6} mol catalyst (1:100), 0.5 ml toluene, 125 °C, 14 h, 2 atm. O₂

**Fig. 4** TEM image of Pt_n-Rh₃ + POM

shape with a very narrow particles size distribution and average size of 2 nm, Fig. 4.

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. Averaged over an area of $1 \mu\text{m}^2$ there showed a ratio of Pt:Zn:Rh:P:V:Mo = 1.0:0.9:1.8:1.2:1.8:10 (experimental) compared to 1:1:1.66:1:2:10 (theoretical) for Pt_n-ZnRh_{12/3}PV₂Mo₁₀O₄₀.

The activity of the two catalysts was compared by turnover number (TON) of the reaction, Table 2. Clearly the use of a Rh(III) counter cation was beneficial in terms of catalytic efficiency. The exchange of the protons in the POM with a metal ion changes the system from an acidic one to neutral one. It should be noted that the use of Na₅PV₂Mo₁₀O₄₀ in place of H₅PV₂Mo₁₀O₄₀ did not lead to stable nanoparticles while use of other counter cations, that is ZnPt_{221/2}PV₂Mo₁₀O₄₀ or ZnRu_{12/3}PV₂Mo₁₀O₄₀ did not lead to improved catalytic results. We can tentatively

conclude that the use of Rh (III) metal cation may provide an additional bimetallic effect; a phenomenon that will be explored more comprehensively in the future.

4 Conclusion

We demonstrated the preparation and characterization of Pt(0) nanoparticles stabilized by acidic POM and neutral (rhodium cation) POM, and studied their catalytic properties in the oxidation of alcohols using molecular oxygen as the only oxidant. Our research reveals that these nanoparticles are easy to prepare, well-defined and good heterogeneous catalysts for the selective oxidation of non-activated secondary alcohols in fairly good yields. A significant improvement in catalysis was achieved by exchanging the protons of the POM with rhodium cations. This points to an additional cooperative effect between the POM, counter cation and the Pt(0) nanoparticles which represent a still to be understood further advantage of this system in the aerobic oxidation of secondary alcohols.

Acknowledgment The research was supported by the Israel Ministry of Science and the Kimmel Center for Molecular Design. R.N. is the Rebecca and Israel Sieff Professor of Organic Chemistry.

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