Heterogeneous $Cs_3PW_{12}O_{40}$ photocatalysts

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Colloidal $Cs_3PW_{12}O_{40}$ shows promise as a heterogeneous photo-oxidant, oxidizing alcohols in aqueous solution upon UV irradiation.

Polyoxotungstate clusters such as the Keggin ion ($XW_{12}O_{40}{}^{n-}$, where X is a heteroatom such as P or Si) are well known thermal catalysts for the oxidative transformation of various organic molecules in solution.[1,2] These species can also function as photocatalysts upon UV irradiation, promoting the oxidation of alcohols to aldehydes or ketones,[3–5] the functionalization of alkanes to form alkenes or ketones,[6] and the dimerization of alkenes.[7] Recent interest in the photochemical properties of these compounds has included the degradation of chlorophenols *via* oxidative processes.[8]

Much work has been done studying polyoxometalates as heterogeneous thermal catalysts and applying them for industrial purposes.[2] However, studies of the photo-oxidative behaviour of polyoxometalates have been with homogeneous solutions. Comparisons of the photo-oxidative activity of these solutions with conventional heterogeneous photocatalysts (*e.g.* TiO_2) have been made.[2d] For many applications, it is desirable to have the photoactive agent in a more recoverable form. Recently, progress has been made with placing polyoxotungstates (soluble forms such as $H_3PW_{12}O_{40}$ or insoluble forms such as $Cs_{2.5}H_{0.5}PW_{12}O_{40}$) on solid supports for liquid phase reactions in order to enhance recovery from the reaction mixture.[9] The utility of the Cs^+ salt for heterogeneous thermal catalysis has been proven.[2,10] There is a need for the potential of these systems for heterogeneous photo-oxidation to be investigated. Here, we demonstrate that a water-insoluble colloid, $Cs_3PW_{12}O_{40}$, can function as an effective photo-oxidative agent for the oxidation of propan-2-ol to acetone.

Colloidal $Cs_3PW_{12}O_{40}$ was synthesized by metathesis of $H_3PW_{12}O_{40}\cdot nH_2O$ and CsCl in H_2O. The precipitate was centrifuged, washed twice with water, and dried at 85 °C. Silica-supported photocatalyst materials were made using the sol–gel procedure of Izumi *et al.*[9a,b] A mixture of 1 g $Cs_3PW_{12}O_{40}$, 3 ml ethanol, 3.5 g tetraethoxysilane (TEOS), and 1.5 g H_2O was heated at 80 °C until dry. The resulting granular material was calcined at 300 °C for 4 h and washed with hot H_2O to separate soluble and fine colloidal materials.

Filtration and light scattering experiments suggested that a large fraction of the unsupported $Cs_3PW_{12}O_{40}$ powder was submicrometer in size, *i.e.* 300 nm in diameter. This value probably represents the size of aggregates of smaller particles as noted previously.[9a] The powder X-ray diffraction patterns of the uncalcined colloid and the calcined $Cs_3PW_{12}O_{40}$–SiO_2 composite were the same, indicating that the crystallinity of the polyoxometalate was not altered significantly during the calcination procedure.[2b,9d] From nitrogen adsorption measurements, it was determined that the $Cs_3PW_{12}O_{40}$ powder had a specific surface area of 126 $m^2\ g^{-1}$, in agreement with previous values.[10c] In comparison, the surface area for TiO_2 (Degussa P25) is 55 $m^2\ g^{-1}$. The calcined, sol–gel supported tungstate material was extremely porous, with a pore size distribution centered at 23 Å, a surface area of 677 $m^2\ g^{-1}$, and a total pore volume of 0.46 ml g^{-1}. This compares favorably with values obtained for the supported thermal catalyst $Cs_{2.5}H_{0.5}PW_{12}O_{40}$–$SiO_2$ and silica gel itself.[9a,b,11]

The insolubility of the $Cs_3PW_{12}O_{40}$ material in water is a critical factor for its potential use for the photo-oxidation of organic species in water, considering the solubility of $H_3PW_{12}O_{40}$. When the granular $Cs_3PW_{12}O_{40}$–SiO_2 composite (several hundred mg in 2 ml H_2O) was stirred at room temperature for *ca.* 3 h, the amount of $PW_{12}O_{40}{}^{3-}$ in the water at the end of this period was *ca.* 3×10^{-7} M as determined by UV–VIS spectroscopy. This was a factor of 100 less than the solubility of uncalcined $Cs_3PW_{12}O_{40}$ in H_2O at natural pH (5–6) and represented a leakage of $< 0.01\%$.

The photochemical oxidation of alcohols by dissolved $PW_{12}O_{40}{}^{3-}$ upon UV irradiation is well documented.[3–5] We demonstrate here that desolubilized polyoxometalate colloids also show photocatalytic behavior. Reflectance spectroscopy was used to observe reduction of the photoexcited $Cs_3PW_{12}O_{40}$ colloid suspended in neat propan-2-ol. An opaque suspension of $Cs_3PW_{12}O_{40}$ in N_2-purged propan-2-ol was irradiated in a 2 mm quartz cell using the output from a 200 W Xe(Hg) arc lamp with a 300 nm cutoff filter. UV–VIS spectral changes in the suspension were monitored using a fibre-optic diffuse reflectance probe coupled to an Ocean Optics S1000 absorption spectrometer. Fig. 1 shows changes in the reflectance spectrum upon irradiation of the slurry. Absorptions in the red region of the visible spectrum are those of the reduced tungstate.[3,4,6d,12] At early irradiation times the absorption maximum is at 760 nm, corresponding to the production of $PW_{12}O_{40}{}^{4-}$. Longer irradiation periods resulted in a blue-shift of the spectral maximum which may be due to > 1 electron reduction at some sites. After irradiation, the blue colloid was allowed to settle. The propan-2-ol liquid phase was uncolored, indicating that bleeding of the desolubilized metalate into solution remained negligible for the reduced forms. Subsequent experiments with silica-supported $Cs_3PW_{12}O_{40}$ yielded similar results under the same conditions. As shown in the figure, reduction is stoichiometrically significant.

This system was also investigated for product formation *via* photo-oxidation of the alcohol. Granules of $Cs_3PW_{12}O_{40}$–SiO_2 (200 mg) were added to 2 ml of 0.5 M aqueous propan-2-ol

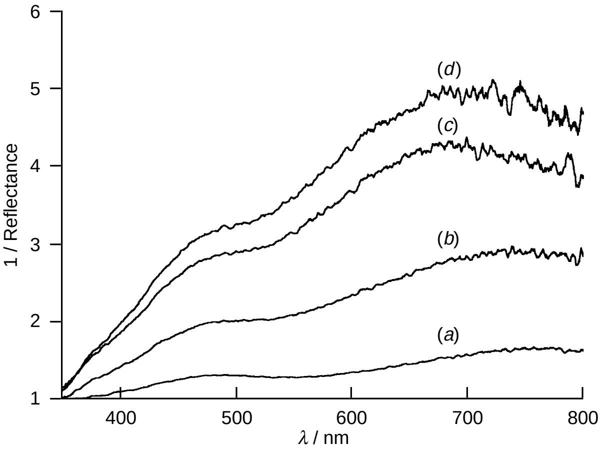

Fig. 1 Visible reflectance spectra for the irradiation (> 300 nm) of an N_2-purged slurry of $Cs_3PW_{12}O_{40}$ in propan-2-ol: (*a*) 7 min, (*b*) 12 min, (*c*) 17 min, (*d*) 22 min

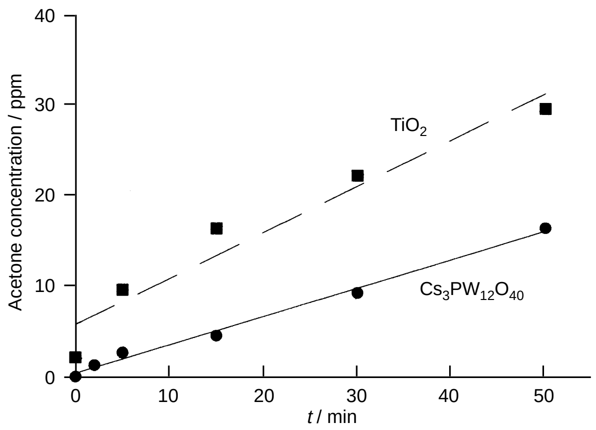

Fig. 2 Production of acetone by the irradiation (254 nm) of $Cs_3PW_{12}O_{40}$ and TiO_2 (2 g l^{-1}) in an aqueous solution (pH 3, $HClO_4$) of propan-2-ol (610 ppm)

(aerated) in a 1 cm quartz cell. The mixture was irradiated with the output of a 200 W Xe(Hg) lamp and 300 nm cutoff filter. The solution was sampled at regular intervals using an HP 5880 GC with FI detector and a 0.53 mm i.d. fused silica column with DB-WAX polyethylene glycol stationary phase (J&W Scientific). Acetone was produced steadily during the irradiation as found previously for dissolved solutions of $PW_{12}O_{40}^{3-}$. In this case formation of the heteropoly blue was not visually evident, due to reoxidation of the metalate by dissolved O_2.[13]

Determination of an accurate quantum yield is not facile, as demonstrated by Sun and Bolton for TiO_2 colloids.[14] However, we have performed a comparative study of the unsupported tungstate with TiO_2 (Degussa-P25), a commercially-available material for photocatalytic oxidations. Equal mass loadings of $Cs_3PW_{12}O_{40}$ or TiO_2 powder (2 g l^{-1}) in a 610 ppm solution of propan-2-ol were placed in an annular quartz cell irradiated by a low pressure mercury lamp (Philips TUV, 15 W, λ = 254 nm). The 4 mm pathlength and irradiation wavelength ensured near-total absorption of photons by the colloidal photocatalysts. The solutions, after allowing 1 h for dark adsorption, were irradiated. Samples were withdrawn and analyzed (GC–FID) for the production of acetone and loss of propan-2-ol. Fig. 2 illustrates the production of acetone by both species. From the data, it appears that the rate of conversion of propan-2-ol to acetone is approximately one-half for $Cs_3PW_{12}O_{40}$ colloid relative to TiO_2. That is, a first unoptimized preparation of a heterogeneous polyoxometalate is very competitive with a widely used form of TiO_2 for photo-oxidation. The apparent reactivity of the tungstate per unit area of catalyst is approximately one quarter that of TiO_2. This is very approximate due to the difficulty of determining the actual surface area illuminated.

The photo-oxidative ability is not limited to alcohols; upon broad-band irradiation [1000 W Xe(Hg) lamp, Pyrex cutoff], an aqueous solution of a model aromatic compound, acetophenone, shows > 99% degradation to hydroxy- and dihydroxyacetophenones over a 3 h period using $Cs_3PW_{12}O_{40}$. This underlines the possible importance of these systems for contaminant degradation, parallel to TiO_2.

In summary, desolubilized polyoxotungstates can function as heterogeneous photocatalysts for the oxidation of organic species in solution. These materials show promise as easily-recovered materials for photochemical oxidations.

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Notes and References

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