Letter

Reduction and recovery of metals from aqueous solutions with polyoxometallates

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Polyoxometallates act as electon relays in a photocatalytic process that involves POM/S/M^{n+} (POM = polyoxometallates $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$ and $P_2Mo_{18}O_{62}^{6-}$; S = organic substrate and M^{n+} = metal ions Ag^+, Cu^{2+}, Pd^{2+} and Ni^{2+}). By a suitable choice of POM and, to a lesser extent, organic substrate, selective photocatalytic reduction of metal ions in aqueous solutions can be achieved.

Metal recovery is a topic of great interest concerning metal pollution and resource conservation, as the demand for certain metals could exceed the known reserves in a few years.[1] Up to now, various methods have been established for the recovery of metals, involving chemical and electrochemical processes. In the last decade, photocatalysis based on TiO_2 particulates has surfaced as a new, potentially useful process for the recovery of metals in a selective way.[2,3]

We present here a novel photocatalytic method for the selective reduction and recovery of several metal ions from their aqueous solutions, based on polyoxometallates (POMs). POMs are a large category of metal oxygen cluster anions with well defined structures and properties, with diverse applications in the fields of analytical chemistry, biochemistry and solid state devices, and have been used as antiviral and antitumor reagents. However, their most important use is in the field of catalysis: POMs, like metal oxides, participate in catalytic processes as oxygen and multielectron relays. Their redox chemistry is characterized by their ability to accept and release a certain number of electrons, in distinct steps, without decomposition.[4] POMs have been termed soluble anodes[5] and indeed they behave as such, especially under irradiation at the O → M CT band (near visible and UV region), oxidizing a great variety of organic compounds,[6] including organic pollutants in aqueous solutions.[7,8] In the process, electrons accumulate on the POM, driving the redox potential to more negative values until a species in solution is able to accept the electrons. At this point it can be said that the POMs are converted to soluble cathodes, able to reduce a diverse number of chemicals. The nature of the POM and the degree of reduction reflect their reducing capability. Thus, H^+ has been reduced to H_2,[9,10] nitrobenzene to aniline,[11] dioxygen to O_2^-,[12] *etc.* In a pioneering photochemical work, Chakley considered using $PW_{12}O_{40}^{3-}$ in the photographic development process, wherein Ag^+ would be reduced to Ag^0.[13]

We report here the ability of photochemically reduced POMs to deliver electrons to a variety of metal ions. By a suitable choice of POM and organic substrate, several metal ions can be reduced to a lower or zero oxidation state. This is in analogy to what has been observed with TiO_2 [2,3] and other metal oxide particulates. Metal ions (M^{n+}) such as Ag^+, Cu^{2+}, Pd^{2+}, Au^{3+}, Hg^{2+}, *etc.*, precipitate out from aqueous solutions through a cyclic process that involves, overall, light-induced ($h^+ + e^-$) separation in TiO_2, followed by hole oxidation of the organic species and electron reduction of metal ions. An advantage offered by POMs, we might say, is that by selecting a POM with appropriate redox potentials and organic substrates whose intermediates do not interfere with the process, selective reduction of metal ions can be achieved. In addition, metal oxide particulates have been reported to be poisoned by deposition of metal ions.[3]

We will present, below, the general behavior of the photolytic system POM/S/M^{n+} (S = organic substrate) and give specific examples concerning the selectivity obtained with this system. We have selected two POMs having a Keggin structure, whose ground state redox potentials vary with the central atom:[14] namely, $PW_{12}O_{40}^{3-/4-}$ (0.221 V *vs.* NHE) and $SiW_{12}O_{40}^{4-/5-}$ (0.057 V *vs.* NHE), as well as $P_2Mo_{18}O_{62}^{6-/8-}$ (0.664 V *vs.* NHE), which has a Wells–Dawson structure. Organic substrates as diverse as 2,4-dichlorophenol (2,4-DCP) and propan-2-ol, whose photodecomposition processes in the presence of POMs are known,[6,7] were chosen for a study of the reduction of Ag^+, Cu^{2+}, Ni^{2+} and Pd^{2+}.

Fig. 1 shows the influence of various metal ions and dioxygen, for comparison, on the decomposition of DCP *vs.* photolysis time of a deoxygenated aqueous solution illuminated using a 320 nm cutoff filter in the presence of $PW_{12}O_{40}^{3-}$.

We have established previously[6] that the photocatalytic cycle for the POM/S/oxidant system proceeds to a steady-state concentration of reduced POM, resulting from the equilibration of the rates of its photoreduction and thermal reoxidation by various oxidants, in our case metal ions, as shown in the following basic reactions:

$$\mathrm{POM} + \mathrm{S} \xrightarrow{h\nu} \mathrm{POM(e^-)} + \mathrm{S_{ox}} \tag{1}$$

$$\mathrm{POM(e^-)} + \mathrm{M}^{n+} \longrightarrow \mathrm{POM} + \mathrm{M}^{(n-1)+} \tag{2}$$

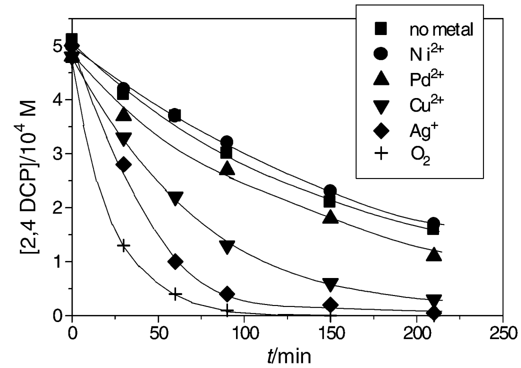

Fig. 1 Photocatalytic decomposition of 2,4-DCP (0.5 mM) from a deaerated aqueous solution in the presence of $PW_{12}O_{40}^{3-}$ (0.07 mM) and the metal ions Ag^+, Pd^{2+}, Cu^{2+} and Ni^{2+} (1.2 mM) or dioxygen for comparison [conditions: pH 1 ($HClO_4$), $\lambda > 320$ nm, $T = 20\,°C$].

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The key reaction for the reduction of metal ions in the photocatalytic cycle is the thermal reaction [eqn. (2)].

Thus, photolysis of the $PW_{12}O_{40}^{3-}/S/M^{n+}$ system proceeds to the steady-state formation of a one-equivalent reduced tungstate, $PW_{12}O_{40}^{4-}$, whose concentration depends on the rates of eqn. (2) (see Fig. 2). When this reaction is very fast (as in the case of Ag^+, Pd^{2+} or dioxygen, for that matter), no blue $PW_{12}O_{40}^{4-}$ is obtained. In contrast, in the presence of Ni^{2+}, which does not reoxidize $PW_{12}O_{40}^{4-}$, the blue color of $PW_{12}O_{40}^{4-}$ develops to a steady-state value that is the same as that observed in the absence of metal ions.

In the case of Cu^{2+}, the reduced catalyst attains a steady-state concentration of a lower value than in the absence of metals or presence of Ni^{2+}. Several thermal experiments between $PW_{12}O_{40}^{4-}$ ($3\text{–}5 \times 10^{-4}$ M) and Cu^{2+} ($5\text{–}25 \times 10^{-4}$ M) at pH 1 (4 ml) indicate rapid reoxidation of $PW_{12}O_{40}^{4-}$ within a subsecond time frame. This reaction did not lead to metallic copper formation, whereas *ca.* 50% of the $PW_{12}O_{40}^{4-}$ reacted with Cu^{2+} ions. This is also observed in the corresponding photocatalytic experiments (Fig. 2), where the concentration of reduced blue $PW_{12}O_{40}^{4-}$ reaches a steady-state value that is *ca.* 50% that observed in the absence of Cu^{2+} ions. This suggests that an equilibrium

$$PW_{12}O_{40}^{4-} + Cu^{2+} \rightleftharpoons PW_{12}O_{40}^{3-} + Cu^{+} \qquad (3)$$

is established, in accordance with the closeness of the one-electron reduction potentials of $PW_{12}O_{40}^{3-/4-}$ and $Cu^{2+/+}$ (0.221 and 0.153 V *vs.* NHE, respectively).

We now show that, using a combination of thermodynamic and kinetic effects, selective precipitation of metal ions can be obtained. Fig. 3 demonstrates the selectivity in the recovery of the metal ions Ag^+, Pd^{2+}, Cu^{2+} and Ni^{2+} when aqueous solutions are subject to photolysis ($\lambda > 345$ nm) in the presence of $PW_{12}O_{40}^{3-}$ and 2,4-DCP. It can be seen that recovery of silver is 100% after 50 min of photolysis, whereas Pd^{2+} is recovered at about 83% after *ca.* 150 min. Under these conditions, copper and nickel do not precipitate out. The reduction of Ag^+ [$E^0(Ag^{+/0}) = 0.799$ V *vs.* NHE] and Pd^{2+} [$E^0(Pd^{2+/0}) = 0.987$ V *vs.* NHE] by $PW_{12}O_{40}^{4-}$ is thermodynamically permitted, whereas that of Ni^{2+} [$E^0(Ni^{2+/0}) = -0.250$ V *vs.* NHE] is not.

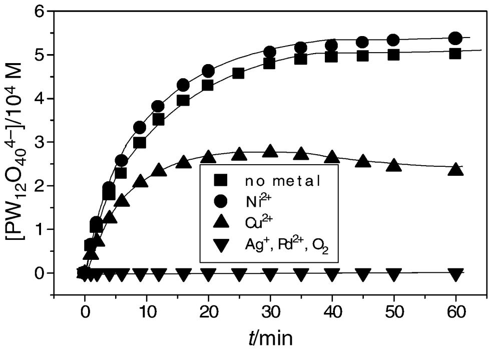

Fig. 2 Steady-state formation of a one-equivalent reduced 12-tungstophosphate, $PW_{12}O_{40}^{4-}$, showing the rate of its reoxidation by M^{n+} [eqn. (2)] upon photolysis of a deaerated aqueous solution of $PW_{12}O_{40}^{3-}$ (0.7 mM), 2,4-DCP (1 mM) and M^{n+} (1.2 mM) [conditions: pH 1 ($HClO_4$), $\lambda > 345$ nm, $T = 20\,°C$].

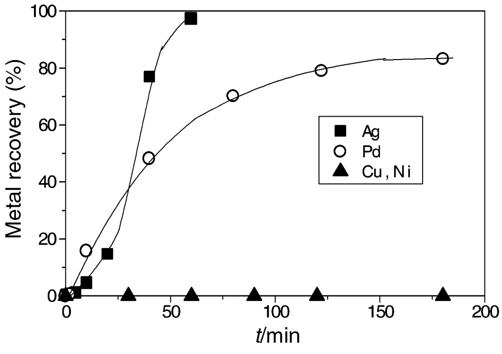

Fig. 3 Recovery of metals through photolysis of a solution containing $PW_{12}O_{40}^{3-}$ (0.7 mM), 2,4-DCP (1 mM) and M^{n+} (1.2 mM) [conditions: pH 1 ($HClO_4$), $\lambda > 345$ nm, $T = 20\,°C$].

The case of Cu^{2+} requires special attention. $PW_{12}O_{40}^{4-}$ is a one-electron donor that reacts rapidly with Cu^{2+} to produce Cu^+, as mentioned earlier. The reaction of Cu^+ with $PW_{12}O_{40}^{4-}$, although thermodynamically favored [$E^0(Cu^{+/0}) = 0.521$ V *vs.* NHE] seems to be slow, requiring higher concentrations of reduced catalyst to proceed at a reasonable rate. Thus, in the photolysis system $PW_{12}O_{40}^{3-}/S/Cu^{2+}$, an induction period is observed for copper precipitation; this period is shortened when the concentration of S is increased to enhance the rate of formation of $PW_{12}O_{40}^{4-}$ [eqn. (1)]. Thus, when the concentration of substrate (2,4-DCP, or propa-2-ol) was 1 mM, about 5% Cu^0 was recovered after 1 h of photolysis, whereas about 36% copper was recovered under otherwise identical conditions (1 mM Cu^{2+}, $\lambda > 320$ nm, pH 1, $T = 18.3\,°C$) when the substrate concentration was increased 10-fold.

Similar results have been obtained with $SiW_{12}O_{40}^{4-}$, except that the overall process was slower. Despite this fact, $SiW_{12}O_{40}^{4-}$ has the advantage of being stable in the pH range *ca.* 0.5 to 5.5.

It should be noted that no reduction of Pd^{2+}, Cu^{2+} and Ni^{2+} is obtained, upon 1 h photolysis, in the absence of either POM or the organic substrate (other conditions as in Fig. 3). In the case of copper, an aqueous solution of 2 mM Cu^{2+} and 2 M propan-2-ol was used). In contrast, illumination of an aqueous solution of Ag^+ and organic substrate precipitates out silver with a rate that is about half of that obtained in the presence of POM.

As far as the 18-molybdodiphosphate is concerned, the two-electron reduced species $P_2Mo_{18}O_{62}^{8-}$ is not reoxidized by dioxygen,[12] so that it was easy to study its reaction with M^{n+} [eqn. (2)] independently. It was shown that $P_2Mo_{18}O_{62}^{8-}$, formed photochemically or otherwise, precipitates Pd^{2+} in a composite reaction process that is at least two orders of magnitude faster than with Ag^+, whereas no reaction takes place with Ni^{2+} and Cu^{2+}, as the reactions with the latter ions are thermodynamically forbidden [$E^0(P_2Mo_{18}O_{62}^{6-/8-}) = 0.664$ V *vs.* NHE].

Thus, by a suitable choice of POM and, to a lesser extent, organic substrate, selective photocatalytic reduction of several metal ions in aqueous solutions can be achieved. Work is in progress to study the photocatalytic mode of reduction of several other metal ions through a combination of various POMs and organic substrates and determine the feasibility of this process in: (i) recovering metals and (ii) possible decontamination of organic pollutants and metal ions from aquatic systems.

Experimental

Deaerated aqueous solutions of the POM ($PW_{12}O_{40}^{3-}$ or $SiW_{12}O_{40}^{4-}$; 0.7 mM), substrate (2,4-DCP or propan-2-ol; 0.5, 1.0 and 10 mM) and 1.2 mM metal ions (as the $CuSO_4$, $NiSO_4$, $PdCl_2$ and $AgNO_3$ salts) were photolyzed with a 1000 W Xe arc lamp (light intensity reduced mechanically by *ca.* 40%) using cutoff filters at 320 and 345 nm to avoid direct photolysis of the substrates. The photolytic process was followed by: (i) recording the decomposition of the organic substrate (2,4-DCP) by HPLC, equipped with a C-18 analytical column and a UV-Vis detector adjusted to 290 nm; the mobile phase consisted of $CH_3CN\text{–}H_2O$, 50 : 50 v/v, in isocratic mode, at a flow rate of 1 ml min^{-1}; (ii) the development of the characteristic blue colors of reduced POM[15] and (iii) analysis of metal ions left in solution or as metallic elements precipitated out after filtration, dissolution in *ca.* 32% HNO_3 (Cu, Ni, Ag) or *aqua regia* (Pd) and analysis by atomic absorption spectrophotometry (monitored at 324.7, 232.0, 338.3 and 247.6 nm, respectively). For the direct study of eqn. (2), a certain amount of $P_2Mo_{18}O_{62}{}^{8-}$ was made by photolysis of an aqueous solution of 0.7 mM $P_2Mo_{18}O_{62}{}^{6-}$ in the presence of 5 M propan-2-ol (pH 1, $HClO_4$). The concentration of reduced molybdate, $P_2Mo_{18}O_{62}{}^{8-}$, was followed spectrophotometrically ($\varepsilon_{756} = 1.1 \times 10^4$ M^{-1} cm^{-1}). A portion of this solution was mixed with a solution of M^{n+} and the process in eqn. (2) was followed by monitoring, at 756 nm, the decoloration of the blue $P_2Mo_{18}O_{62}{}^{8-}$.

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