

## Potential applications of solar reactions photocatalysed by the decatungstate anion

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### ABSTRACT

Two potential applications of photocatalysed reactions in the presence of the decatungstate anion  $W_{10}O_{32}^{4-}$  under solar light irradiation were explored. Firstly, we investigated the possibility offered by alkane functionalisation. By irradiation with  $[(t\text{But})_4\text{N}]_4W_{10}O_{32}$ , cyclohexane was converted into cyclohexanone and cyclohexane hydroperoxide, which give cyclohexanol after reduction. A small amount of polyoxygenated products is also formed. Secondly, we studied the potential of  $Na_4W_{10}O_{32}$  to act as a photocatalyst for water depollution processes. Several phenols and pesticides, especially atrazine, were used as substrates and the results were compared to those obtained in the presence of  $TiO_2$ . Since neither  $TiO_2$  nor  $Na_4W_{10}O_{32}$  lead to the total mineralisation of atrazine, we made an attempt for integrating photo- and biodegradation processes in order to achieve the total mineralisation of the pollutant.

Keywords : photocatalysis, polyoxometalate, alkane functionalization.

### RESUME

Deux applications potentielles des réactions photocatalysées par l'anion decatungstate  $W_{10}O_{32}^{4-}$  sous irradiation solaire ont été explorées. Premièrement, nous avons examiné les possibilités offertes pour la fonctionnalisation des alcanes. Par irradiation en présence de  $[(t\text{But})_4\text{N}]_4W_{10}O_{32}$ , le cyclohexane est converti directement en cyclohexanone et en hydroperoxyde, qui produit après réduction du cyclohexanol. Une petite quantité de produits polyoxygénés est également formée. Deuxièmement, nous avons étudié les potentialités d'action de  $Na_4W_{10}O_{32}$  en tant que photocatalyseur pour la dépollution des eaux. Différents phénols et pesticides, dont l'atrazine, ont été utilisés comme substrats et les résultats comparés à ceux obtenus en présence de  $TiO_2$ . Ni  $TiO_2$ , ni  $Na_4W_{10}O_{32}$  ne conduisant à la minéralisation de

l'atrazine, nous avons essayé d'intégrer photo- et biodegradation dans le but d'obtenir la minéralisation totale du polluant.

**Mots-clés** : photocatalyse, polyoxométallate, fonctionnalisation d'alcanes.

## INTRODUCTION

Polyoxometalates are materials that draw more and more interest. The number of publications devoted to their synthesis, structure and properties is rapidly increasing [1]. Some polyoxometalates are well known for their photocatalytic activity in the oxidation of substrates such as alkanes, alcohols, **alkenes** [1,2]. We selected the decatungstate anion  $W_{10}O_{32}^{4-}$  for its absorption spectrum tailing into the visible, overlapping the near UV solar emission spectrum. We investigated two different types of solar photocatalysed reactions: the photooxidation of alkanes and the photodecomposition of pollutants in water. Photooxidation of alkanes, leading to products with higher value than the starting materials, could be interesting in the synthesis of nylon for example, concerning hexane as the initial **alkane** substrate. The use of polyoxometalates for the photocatalytic degradation of phenols was investigated recently [3,4]. Depollution processes using semiconductor particles, **like**  $TiO_2$  were widely investigated [5,6,7]. However, they sometimes remain unable to lead to the total mineralisation of the pollutants [8]. We compared the kinetics of solar photodegradation of different compounds in the presence of  $Na_4W_{10}O_{32}$ , in the presence of  $TiO_2$  and under **direct** photolysis. We also studied the possibility of integrating photo- and biodegradation in order to achieve the total mineralisation of a widely used pesticide, atrazine.

## EXPERIMENTAL SET-UP

Experimental procedures for fonctionnalisation of alkanes [9], photodecomposition of pollutants [10] and biodegradation [11] have been published elsewhere.

## RESULTS AND DISCUSSION

### *Alkane functionalization*

After preliminary experiments in the photooxidation of **adamantane** (Ad) [9], we

irradiated 4 L of 5% cyclohexane/acetonitrile solution containing  $5.5 \cdot 10^{-4}$  mol L<sup>-1</sup> [(tBut)<sub>4</sub>N]<sub>4</sub>W<sub>10</sub>O<sub>32</sub> during one week. The decrease of the cyclohexane concentration

against the delivered sun energy follows a first order kinetics even after addition of 150 mL of cyclohexane on the third day of irradiation (Figure 1). The catalyst can be used for at least one week (Figure 1). As in the case of Ad [9], the peroxides formation, which also follows a first order kinetics, was measured by iodometric titrations (Figure 2). In the Figures 3 and 4, the cyclohexanol and cyclohexanone ratio evolutions (after reduction with trimethylphosphite of 1 ml aliquots of the reaction mixture and GC analysis) are reported against the delivered sun energy. The rate of the formation of cyclohexanol increases at the beginning of the reaction then is lowered, not due to the fatigue of the catalyst but to the fact that the cyclohexane hydroperoxide is very reactive towards the photoexcited catalyst and gives subsequent side reactions. The formation of cyclohexanone, very slow, decreases because the excited photocatalyst is more reactive towards the cyclohexanone than the cyclohexane. After one week of irradiation, more than 90 % of the starting cyclohexane has been oxidized.

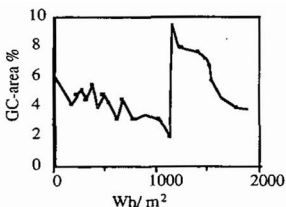


Figure 1: Cyclohexane evolution

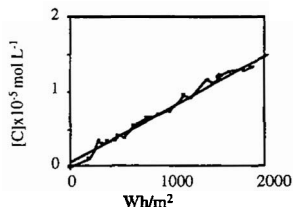


Figure 2: Total peroxide formation

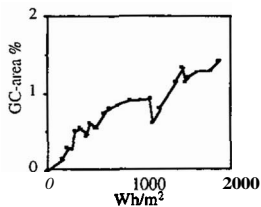


Figure 3: Cyclohexanol formation

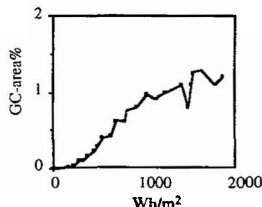


Figure 4: Cyclohexanone formation

*Solar photodegradation of water pollutants*

Different phenols (phenol, 4-chlorophenol, 2,4-dichlorophenol) and pesticides (atrazine, bromoxynil, imidachloprid and oxamyl) were tested. Figure 5 shows for example the evolution of the concentration of atrazine versus the solar irradiation energy during direct photolysis (a), photocatalysis in the presence of  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  (b), and in the presence of  $\text{TiO}_2$  (c). For all the substrates, photodegradation under direct photolysis was slower than photodegradation in the presence of any of the photocatalysts. In the case of atrazine, we observed that the order of reactivity for the degradation of the pollutant was  $\text{TiO}_2 > \text{Na}_4\text{W}_{10}\text{O}_{32}$ . Similar order of reactivity was obtained for the other pure organic compounds (phenol, 4-chlorophenol, 2,4-dichlorophenol, bromoxynil, pure imidachloprid). On the contrary, the rate of the photodecomposition of formulated oxamyl is similar in the presence of both photocatalysts and in the case of formulated imidachloprid, it is greater in the presence of  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  than in the presence of  $\text{TiO}_2$ . The effect of the presence of surfactants is discussed elsewhere [10].

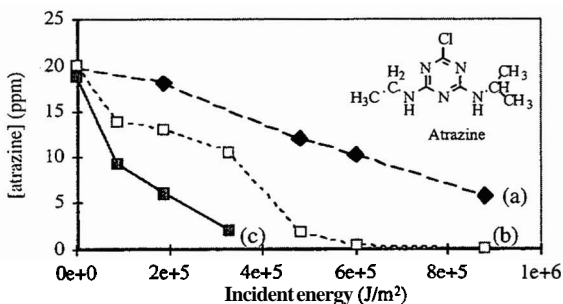


Figure 5: Solar photodegradation of 20 ppm atrazine ( $9.2 \cdot 10^{-3} \text{ mol/L}$ ) in acidic aqueous solution ( $\text{HClO}_4$ ,  $\text{pH}=2.2$ ) (a) under direct photolysis, (b) in the presence of  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  ( $1.5 \cdot 10^{-3} \text{ mol L}^{-1}$ ), (c) in the presence of  $\text{TiO}_2$  ( $0.2 \text{ g L}^{-1}$ ).

Concerning the mineralisation of the substrates,  $\text{TiO}_2$  appears to be far more efficient than  $\text{Na}_4\text{W}_{10}\text{O}_{32}$ . Photocatalysed mineralisation soon follows the photodegradation of the substrate during photocatalysis in the presence of  $\text{TiO}_2$

(except atrazine for which total mineralisation is not achieved [8]). In the presence of  $\text{Na}_4\text{W}_{10}\text{O}_{32}$ , nearly no mineralisation occurs during one day of solar irradiation, whatever the substrate.  $\text{TiO}_2$  was chosen as a reference photocatalyst in these experiments because it has been already widely studied and appears as one of the most efficient photocatalytic process since now [5,6,7]. However, it is heterogeneous whereas  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  is homogeneous. The comparisons between both are thus limited and the degradation mechanisms appear to be quite different [10,11].

### *Integrating photo and biodegradation*

Photocatalysed degradations of atrazine in the presence of either  $\text{TiO}_2$  [11,12] or  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  [11] were studied elsewhere. These photocatalysed processes are not able to break the aromatic ring of the molecule, which structure is drawn on Figure 5. However, they lead partly to the **dechlorination** of the pollutant, which is a key step of the degradation pathway, since the dechlorinated **intermediates** loose the phytotoxicity of the pesticide [13]. Very few micro-organisms are able to perform these dehalogenation reactions [14,15]. We then investigated the integration of photo- and biodegradation processes, using  $^{14}\text{C}$  ring-labelled atrazine. After 32 hours of lamp irradiation, either in the presence of  $\text{TiO}_2$  or  $\text{Na}_4\text{W}_{10}\text{O}_{32}$ ,  $^{14}\text{C}$  ring-labelled aqueous atrazine solutions are incubated with three different micro-organisms strains : *Phanerochaete chrysosporium*, *Bacillus licheniformis*, *Penicillium chrysogenum*. The most interesting results are obtained with this last strain. After 1 week of incubation, 20 % of the photodegraded  $\text{TiO}_2$  solutions and 27 % of the photodegraded  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  solutions are mineralised [11].

## CONCLUSION

The decatungstate anion, and **polyoxometalates** in general, are promising materials in view of new applications. We demonstrated here the photocatalytic potentialities of  $\text{W}_{10}\text{O}_{32}^{4-}$  under solar irradiation. This anion can be used in photocatalytic reactions either in view of synthesis (like alkane fonctionnalisation) or depollution

applications. In this last case, it can be used alone or combined with biodegradation processes. In order to go further into the development of potential new applications, a better insight into the mechanisms of these photocatalysed reactions is necessary. Moreover, incorporation of the decatungstate anion in films or its fixing onto rigid **supports** or matrices seems to be unavoidable to separate easily the catalyst from the reaction products. The reactivity of the supported materials **might** be in this case quite different than this in solution. Studies dealing with the synthesis of supported polyoxometalates have been recently published [16,17,18] and the use of these supported photocatalysts is worth while being studied.

## ACKNOWLEDGEMENTS

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