Research Note

Selective photooxidation of diols with silica bound $W_{10}O_{32}^{4-}$

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Abstract

The decatungstate anion $W_{10}O_{32}^{4-}$ has been heterogenized on silica previously functionalized with different ammonium cations covalently bound to the surface of the solid support. These materials are investigated as photocatalysts for the oxygen-assisted oxidation of 1,3-butanediol and 1,4-pentanediol. Product distribution and adsorption experiments indicate that the polarity of the environment surrounding the photoactive anion plays a crucial role in controlling the adsorption of diols on the surface and, consequently, their reaction with the photoexcited decatungstate. Proper reaction conditions are found for obtaining more than 90% of 4-hydroxy-2-butanone from 1,3-butanediol and for stopping the oxidation of 1,4-pentanediol to 4-hydroxypentanal with good yield. The employed photocatalysts present a very good stability in repeated experiments.
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1. Introduction

Heterogenization of polyoxoanions for photocatalytic oxidations by molecular oxygen has attracted much attention in the last years. In particular, heterogenization of the decatungstate $W_{10}O_{32}^{4-}$ for photooxidation reactions has been previously performed following different procedures, such as by impregnation of a solid support [1–4], by embedding in polymeric membranes [5–7] or inside the silica network [8,9]. Generally speaking, the support makes the photocatalyst more easily handled and recycled, it allows a free choice of the reaction medium and, sometimes, it controls efficiency and selectivity of the processes.
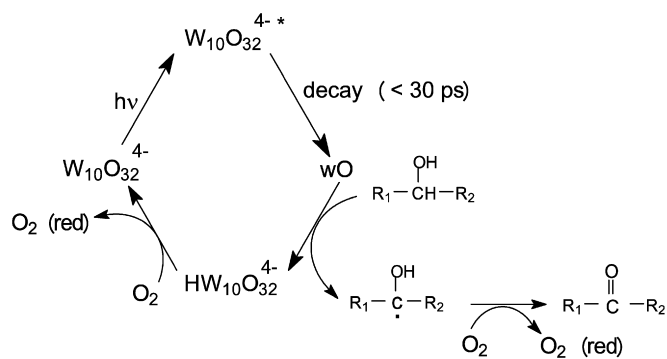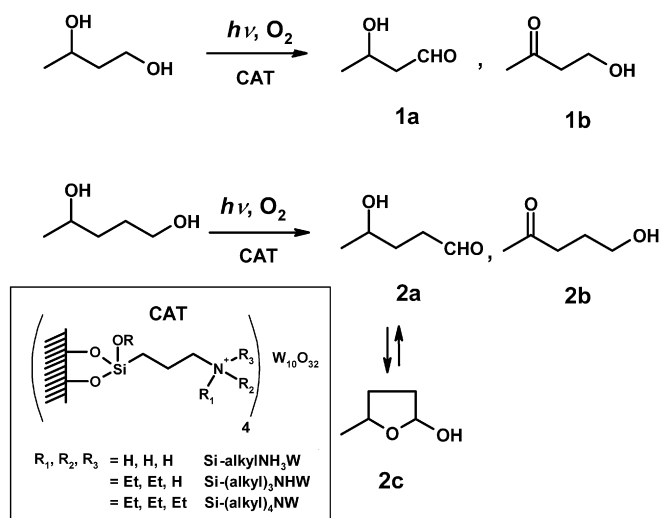
One of the present authors has recently reported [10] that decatungstate $W_{10}O_{32}^{4-}$ can be heterogenized with silica previously functionalized with different ammonium cations covalently bound on the surface of the solid support. The polyoxoanion is immobilized on the solid surface through an exchange reaction by mixing the selected surface bound alkylammonium salt and an aqueous solution of $Na_4W_{10}O_{32}$. It has been found

that the so obtained systems allow one to expand the reaction solvent choice and present high efficiency and selectivity in the catalytic oxidation of sulfides by hydrogen peroxide [10]. In the present paper these materials are investigated as photocatalysts for the oxygen-assisted oxidation of one site of multifunctional molecules such as diols. We were prompted to explore this strategy because now it is well-established that $W_{10}O_{32}^{4-}$ is able to induce the photocatalytic oxidation of alcohols in homogeneous solution as briefly summarized in the following [1,7,11–15]. It is to outline that the preferential oxidation of one of the alcoholic functionalities present in diols, with production of hydroxyaldehydes or hydroxyketones as the main products, is an important transformation in synthetic organic chemistry [16].

Previous studies indicate that the photocatalytic oxidation of alcohols by $W_{10}O_{32}^{4-}$ occurs according to Scheme 1 [1,7, 11–15]. It is generally accepted that illumination of the decatungstate yields an oxygen to metal charge transfer excited state ($W_{10}O_{32}^{4-}$*), which decays rapidly to a reactive transient designed as wO. This intermediate reacts with aliphatic and aromatic alcohols, through hydrogen atom abstraction mechanism, leading to the reduced form of decatungstate ($HW_{10}O_{32}^{4-}$) and to an organic radical [15]. The photocatalytic process leads to the formation of a carbonyl compound as a conse-

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Scheme 1. Photocatalytic behaviour of $W_{10}O_{32}^{4-}$.

Scheme 2. Oxidized products obtained upon irradiation of heterogeneous $W_{10}O_{32}^{4-}$ suspended in CH_2Cl_2 solutions containing the diol in the presence of O_2.

quence of the reaction of this radical with O_2, which also provides the reoxidation of the photoreduced decatungstate. In any case, O_2 undergoes reduction to reactive oxygenated species [1,7,15].

In the $W_{10}O_{32}^{4-}$-based materials employed in this work the decatungstate is held on the support by its ionic bond with tetraalkylammonium cations in Si-(alkyl)$_4$NW, with trialkylammonium cations in Si-(alkyl)$_3$NHW and with monoalkylammonium cations in Si-alkylNH$_3$W (see insert in Scheme 2). The structure of these three materials has been previously investigated through different physical–chemical techniques [10], which evidenced that (i) the structure of the decatungstate is still preserved on the silica surface; (ii) the loading of the decatungstate is in the range 0.06–0.13 mmol/g; (iii) the decatungstate anion is bound to the solid support through ionic interactions with four supported ammonium cations, since the presence of sodium was not detected in the catalysts. Attention is here focused on the effects of the decatungstate counterion in controlling the microenvironment where the photocatalytic process occurs and, consequently, its chemo- and regioselectivity. The diols investigated as oxidizable substrates are 1,3-butanediol and 1,4-pentanediol.

2. Experimental

The decatungstates $Na_4W_{10}O_{32}$ and $(n\text{-}Bu_4N)_4W_{10}O_{32}$ were prepared following literature procedures [17]. The photocatalysts Si-(alkyl)$_4$NW, Si-(alkyl)$_3$NHW and Si-alkylNH$_3$W were synthesized as previously described [10]. The preparation of anchored primary and tertiary ammonium salts was performed by reacting silica (5 g) and the suitable (alkylaminopropyl)trialkoxysilane (10 mmol) in toluene at reflux. After washing and drying under vacuum (60 °C), the resulting materials in dichloromethane (5 g in 25 ml) were reacted with trifluoromethane sulfonic acid (two equivalents respect to the supported amino group) at room temperature, filtered off, washed and dried. To prepare supported quaternary ammonium salt, bromopropylated silica was first obtained condensing (bromopropyl)trimethoxysilane (10 mmol) with silica silanols (5 g) by refluxing in toluene and then treated with triethylamine (50 mmol). The solid was filtered off, washed and dried. Immobilization of $W_{10}O_{32}^{4-}$ was carried out by stirring a mixture of the selected surface bound alkylammonium salt (4 mmol) and an aqueous solution of sodium decatungstate (4 mmol) at room temperature for 30 min. The white solids were filtered off, carefully washed with distilled water, ethanol, diethyl ether and with hot acetonitrile using a Soxhlet apparatus. The dried materials were characterized as previously reported [17]. Photochemical excitations were performed with a Helios Italquartz Q400 medium-pressure mercury lamp selecting wavelengths with cut-off filters. Products analysis were carried out by using a HP 6890 gas chromatograph, equipped with a flame ionization detector and a DB-WAX capillary column. Quantitative analyses was performed with calibration curves obtained with authentic samples or prepared ones. For CO_2 determination a pH meter BasiC 20 CRISON equipped with a gas sensing probe (Crison 9666) was employed. When necessary, UV–vis spectra were recorded with a KONTRON Uvikon 943 spectrophotometer. Si-(alkyl)$_4$NW, Si-(alkyl)$_3$NHW and Si-alkylNH$_3$W were dispersed in 3 ml (7 g/l) of a CH_2Cl_2 or CH_3CN solution containing 1,3-butanediol or 1,4-pentanediol (0.01 M). The obtained suspensions were stirred and irradiated with wavelengths higher than 290 nm, at room temperature and under 760 Torr of O_2. On the basis of previous investigations, the amount of 7 g/l of supported decatungstate was the optimum in order to ensure the maximum absorption of light [2,4] and was chosen for all the photocatalysts. After irradiation, sample was centrifuged, the products that remained eventually adsorbed on the irradiated powder were extracted with CH_2Cl_2 (2×3 ml) and analysed. Homogeneous reactions were carried out dissolving $(n\text{-}Bu_4N)_4W_{10}O_{32}$ in CH_3CN solutions containing the diol (0.01 M). The decatungstate concentration in the final solution (2×10^{-4} M) warranted the complete absorption of all the incident photons. Three ml of this solution were irradiated (20 min) with wavelengths higher than 290 nm, at room temperature and under 760 Torr of O_2. After irradiation, the organic phase was analysed by gas chromatography. Each photocatalytic experiment was repeated three times in order to evaluate the errors, which never exceeded ±5%. No oxidation products were obtained when blank experiments were run in the dark

or irradiating without the photocatalysts. Evaluation of the adsorption of the two diols on the surface of photocatalysts was carried out suspending each photocatalyst (7 g/l) in 3 ml of the CH_2Cl_2 solution containing the diol (0.01 M) and keeping it in the dark for 15 min under magnetic stirring. The amount of diol adsorbed was established considering its decrease in the solution. Analogous experiments were performed with solutions containing mixtures of 1-pentanol/2-pentanol (0.005 M each) and 1-butanol/2-butanol (0.005 M each). Evaluation of the adsorption of carboxylic acids or carboxylates on the photocatalysts was carried out suspending each photocatalyst (7 g/l) in 3 ml of a CH_2Cl_2 solution containing 4-oxopentanoic acid or 3-hydroxybutiric acid (0.005 M) and keeping it in the dark for 20 min under magnetic stirring. The amount of carboxylic acid adsorbed was established measuring its decrease in the solution by GC analysis; the possible release of the decatungstate in the solution phase was evaluated by UV–vis analysis of the solution.

3. Results and discussion

Dichloromethane suspensions of Si-(alkyl)$_4$NW or Si-(alkyl)$_3$NHW or Si-alkylNH$_3$W (7 g/l) containing 1,3-butanediol were irradiated ($\lambda > 290$ nm) at room temperature and under 760 Torr of O_2. Twenty minutes irradiation caused the conversion of the diol to 3-hydroxybutanale (**1a**) and 4-hydroxy-2-butanone (**1b**) (see Scheme 2), which derive from the oxidation of primary or secondary alcoholic functionality of the diol. Specifically, these two products represented more than 90% of the oxidized 1,3-butanediol and gave reason of about 90% of the overall gas chromatographic area of the obtained photoproducts. Analogous photocatalytic experiments indicated that 1,4-pentanediol (0.01 M) could be converted to 4-hydroxypentanal (**2a**) and 5-hydroxy-2-pentanone (**2b**). Other two chromatographic peaks have been attributed to the cyclic emiacetalic diastereoisomers (**2c**) derived from the closure of **2a**. Minor amounts of unidentified compounds likely due to further photooxidation processes were also formed. **2a**, **2b** and **2c** represent about 80% of the overall gas chromatographic areas of the detected products. We could estimate that the mass balance between the detected products and diol disappeared was about 90% also for this diol.

Carbon dioxide, deriving from complete oxidative degradation of the substrate, must be counted among the possible reaction products in photocatalysis with polyoxoanions [18]. While this is an advantage in the abatement of pollutants, it is a drawback in the present case, where the aim is the accumulation of valuable reaction intermediates. Some specific experiments carried out in a closed reactor in order to collect the CO_2 eventually formed enable us to conclude that carbon dioxide was not formed in detectable amounts during the photocatalytic oxidation of both 1,3-butanediol and 1,4-pentanediol. We have also verified that no oxidation products were obtained when blank experiments were run in the absence of light or irradiating the dispersing medium without the photocatalysts.

On the basis of the described results, we can state that the well known ability of photoexcited $W_{10}O_{32}^{4-}$ to induce alcohol

Table 1
Photocatalytic properties[a] of heterogenized decatungstate in the oxidation of 1,3-butanediol and of 1,4-pentanediol in CH_2Cl_2

Diol	Photocatalyst	$n\mathbf{a}$[b] (μmoles of aldehyde)	$n\mathbf{b}$[b] (μmoles of ketone)	$n\mathbf{a}/n\mathbf{b}$
1,3-butanediol ($n = 1$)				
	Si-(alkyl)$_4$NW	0.1	1.6	0.06
	Si-(alkyl)$_3$NHW	0.2	1.1	0.18
	Si-alkylNH$_3$W	0.76	1.2	0.63
1,4-pentanediol ($n = 2$)				
	Si-(alkyl)$_4$NW	3.0	1.0	3.0
	Si-(alkyl)$_3$NHW	1.6	0.4	4.0
	Si-alkylNH$_3$W	1.5	0.2	7.5

[a] In a typical experiment the employed photocatalyst (7 g/l) was suspended in a CH_2Cl_2 solution (3 ml) containing 1,3-butanediol or 1,4-pentanediol (0.01 M) and irradiated (20 min, $\lambda > 290$ nm) at 298 ± 1 K and 760 Torr of O_2. Reported values are the mean of three repeated experiments and are $\pm 5\%$.
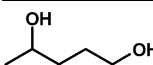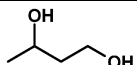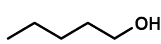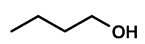
[b] Amount of carbonylic compounds as μmoles obtained in 3 ml of solution.

oxidation through Scheme 1 [1,7,11–15] is retained also after its heterogenization on silica. The nature of the photoproducts is consistent with the oxidation of one alcoholic functionality of the diol, although two-site attack has been suggested as important in the oxidation of diols in conventional electrolytic cells [19]. It is noteworthy that, for both the investigated diols, partially oxidized product can be accumulated in good yields with no formation of ketoacids and no mineralization of the substrate to carbon dioxide.

As far as the stability of the photocatalysts is concerned, UV–vis spectra demonstrated that the decatungstate anion was not released in detectable amounts into the solution during the photocatalytic experiment, thus confirming that we were in the presence of real heterogeneous catalytic processes. We have also experimental evidence that the loss of activity of the three photocatalysts in terms of detected end products was less than 15% after five repeated cycles. This slow deactivation may be tentatively ascribed to the degradation of $W_{10}O_{32}^{4-}$ to form small undetectable fragments. Control experiments allowed us to rule out the possibility that small amounts of photogenerated carboxylic acids and carboxylates may produce ion exchange in some extent. In fact, (i) GC analysis indicates that the concentration of 4-oxopentanoic acid or 3-hydroxybutiric acid in CH_2Cl_2 solutions (0.005 M) did not decrease after contact with the solid photocatalysts and (ii) UV–vis spectra gave evidence that the decatungstate was not released in detectable amounts into the solution phase.

Table 1 compares the photocatalytic activities of Si-(alkyl)$_4$NW, Si-(alkyl)$_3$NHW and Si-alkylNH$_3$W dispersed in CH_2Cl_2 in the oxidation of 1,3-butanediol and 1,4-pentanediol. Columns 3 and 4 report the μmoles of aldehyde (**na**) and ketone (**nb**) obtained for both the investigated diols. In the case of 1,4-pentanediol, **2a** is the sum of 4-hydroxypentanal and of its cis-trans emiacetalic isomers (**2c**, see Scheme 2) which are formed by cyclization of the aldehyde and remain in equilibrium with it. In the last column the concentration ratio between aldehyde and ketone enable us to evaluate how much the nature

Table 2
Adsorption % of diols and monoalcohols on photocatalysts

Photocatalyst	Adsorption (%)[a]					
	1,4-pentanediol	1,3-butanediol	1-pentanol	2-pentanol	1-butanol	2-butanol
Si-(alkyl)$_4$NW	10	8	4	4	<1	<1
Si-(alkyl)$_3$NHW	12	9	10	9	2.8	2.1
Si-alkylNH$_3$W	19.8	22.4	13	8	8.5	6.5

[a] In a typical experiment the photocatalyst (7 g/l) was suspended under magnetic stirring for 15 min in a CH$_2$Cl$_2$ solution containing the diols or mixtures of their monofunctional models. Columns 2 and 3: 1,4-pentanediol or 1,3-butanediol, respectively (0.01 M). Column 4: a mixture of 1-pentanol and 2-pentanol (0.005 M each). Column 5: a mixture of 1-butanol and 2-butanol (0.005 M each).

of the counterion bound on the solid support affects the relative reactivity of the two alcoholic functional groups.

Previous studies regarding kinetic and mechanistic aspects of photocatalysis by $W_{10}O_{32}^{4-}$ have demonstrated that the primary reaction between wO and alcoholic substrates involves hydrogen-atom abstraction from the C–H bond α to the OH group (Scheme 1) [11–15]. From this point of view, both the primary and the secondary alcoholic functions of 1,3-butanediol and of 1,4-pentanediol can undergo hydrogen-atom abstraction by wO from both the α C–H bonds. Since this reaction leads to carbon centered radicals, the preferential oxidation of the secondary carbon to give a ketone would be predicted on the basis of pure thermodynamic considerations [15]. On the other hand, it is seen in Table 1 that the ratio between aldehyde and ketone depends on the nature of the counterion. Specifically, this ratio increases markedly as the alkyl chains of the cation are substituted by hydrogen atoms. Interestingly enough, we note that optimal conditions have been found in CH$_2$Cl$_2$ for obtaining more than 90% of 4-hydroxy-2-butanone (1b) from 1,3-butanediol (with Si-(alkyl)$_4$NW) and about 90% of 4-hydroxypentanal (2a) and its cyclic emiacetalic isomers (2c) from 1,4-pentanediol (with Si-alkylNH$_3$W).

The observed effect of the counterion on the regioselectivity of the photoprocess suggests that a first important parameter affecting the reactivity of the investigated photocatalysts may be the polarity of the solid surface and, consequently, its interaction with the diol: preferential adsorption effects can be significant in controlling the selectivity, considering that the region of the molecule which is more closely associated with the surface and near to the photoexcited decatungstate is expected to undergo more rapid oxidation. In particular, the enhanced polarity of the surface due to the presence of hydrogen atoms instead of alkyl chains should favour the preferential adsorption of the primary OH group of the more hydrophilic head of the diol molecule with respect to the secondary OH group of its more hydrophobic tail, thus fostering the interaction of the primary alcoholic group with the photoexcited decatungstate and, consequently, its oxidation. This statement is supported by a previous investigation by Fox et al. on the oxidation of 1,4-pentanediol by photoexcited TiO$_2$ where they attributed the observed regioselective oxidation of the primary OH group to a site selective adsorption on the polar surface of the active photocatalyst [20].

Some experiments were carried out suspending each heterogeneous photocatalyst in a CH$_2$Cl$_2$ solution containing 1,3-bu-

tanediol or 1,4-pentanediol and evaluating the amount of diol adsorbed after 15 min. It is seen in columns 2 and 3 of Table 2 that the adsorption of both 1,3-butanediol and 1,4-pentanediol occurs in the order Si-alkylNH$_3$W > Si-(alkyl)$_3$NHW > Si-(alkyl)$_4$NW, indicating that the enhanced polarity of the surface due to the presence of hydrogen atoms instead of alkyl chains favours the adsorption of the diols. Analogous experiments (columns 4 and 5 of Table 2) were carried out suspending the photocatalysts in CH$_2$Cl$_2$ solutions containing mixtures of monofunctional alcohols simulating the two different hydroxy functional groups present in the diols: 1-pentanol and 2-pentanol for 1,4-pentanediol (column 4), 1-butanol and 2-butanol for 1,3-butanediol (column 5). The results obtained confirm that adsorption phenomena play a key role in controlling the regioselectivity of the $W_{10}O_{32}^{4-}$-assisted photooxidation of 1,3-butanediol or 1,4-pentanediol. In fact, Table 2 shows that primary alcohols are adsorbed in a greater extent than are secondary substrates and, therefore, they can interact easily with the photoexcited $W_{10}O_{32}^{4-}$. The adsorption of both 1-butanol and 2-butanol become negligible on the less polar photocatalyst Si-(alkyl)$_4$NW.

The results of Table 1 show that the selectivity of the primary alcohol oxidation is higher for 1,4-pentanediol than for 1,3-butanediol, in line with the fact that this regioselectivity is expected to be higher when the two competitive sites are more distant each other. In order to evaluate the possibility that the regioselective oxidation of 1,4-pentanediol to 4-hydroxypentanal can be also controlled by the nature of the solvent, other photocatalytic experiments were performed using CH$_3$CN as dispersing medium. We have experimental evidences that, when the photocatalytic experiments were carried out in this solvent the concentration ratios between aldehyde and ketone were always lower (in the range 0.6–0.7) than those obtained in CH$_2$Cl$_2$ independently of the photocatalyst employed (see Table 3 as supplementary material). A plausible explanation is that the more polar CH$_3$CN reduces the diol adsorption and, consequently, the above described surface effects. Accordingly, adsorption experiments confirm that the monoalcohols models of 1,4-pentanediol were only slightly adsorbed on all the employed photocatalysts when dissolved in CH$_3$CN (<3%).

The activity of the investigated heterogeneous photocatalysts can not be compared with that of $W_{10}O_{32}^{4-}$ in homogeneous solution from a quantitative point of view since (n-Bu$_4$N)$_4$W$_{10}$O$_{32}$, which is the salt usually employed for obtaining homogeneous solutions, is not soluble in CH$_2$Cl$_2$.
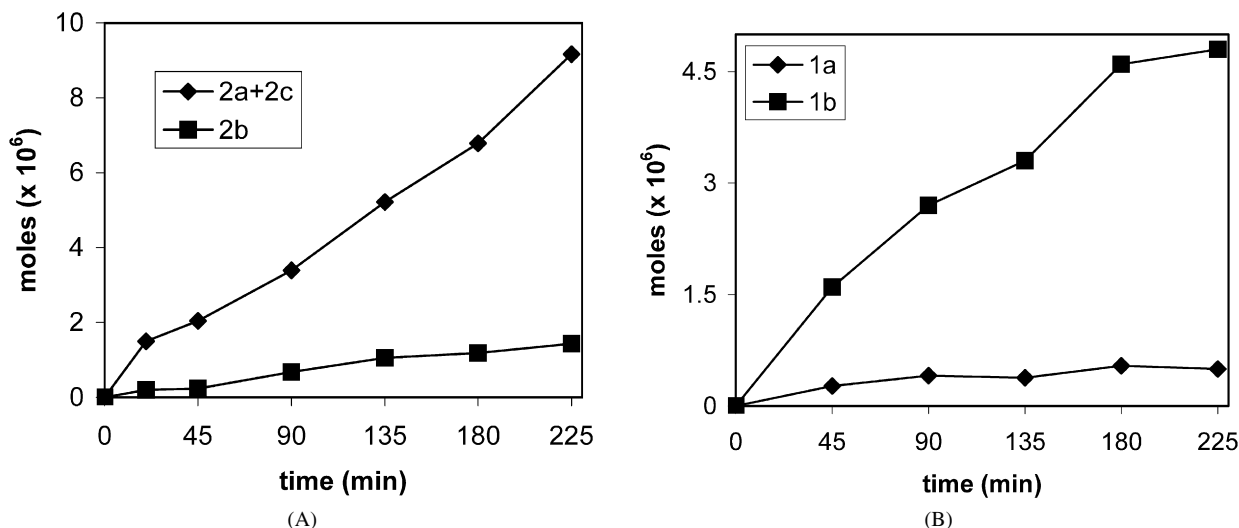
Fig. 1. μmoles of products vs time obtained irradiating ($\lambda > 290$ nm, 298 K, 760 Torr of O_2) (A) Si-alkylNH$_3$W (7 g/l) in CH$_2$Cl$_2$ solutions containing 1,4-pentanediol (0.01 M). (B) Si-(alkyl)$_4$NW (7 g/l) in CH$_2$Cl$_2$ solutions containing 1,3-butanediol (0.01 M).

Moreover, the microenvironment variations due to the size and the nature of the counterions that occur on the surface are not reproducible in the homogeneous medium. However, a semiquantitative comparison of the photocatalytic properties of Si-(alkyl)$_4$NW, Si-(alkyl)$_3$NHW and Si-alkylNH$_3$W with that of (n-Bu$_4$N)$_4$W$_{10}$O$_{32}$ merits to be done for evaluating the potential future applications of silica bound decatungstate in photocatalysis. In these experiments we were forced to employ CH$_3$CN in order to dissolve (n-Bu$_4$N)$_4$W$_{10}$O$_{32}$. Irradiation (20 min, $\lambda > 290$ nm) of CH$_3$CN solutions of (n-Bu$_4$N)$_4$W$_{10}$O$_{32}$ (2×10^{-4} M) containing 1,3-butanediol or 1,4-pentanediol (0.01 M) led to the formation of the same products obtained in heterogeneous conditions with about the same total overall yield. This is a good result in view of the employment of the silica bound W$_{10}$O$_{32}^{4-}$ in heterogeneous catalysis, where, usually, a significant loss of activity in comparison with the homogeneous phase is observed. Lack of surface effects and restriction in choice of the solvent have a negative effect on the selectivity. In fact, we found that the concentration ratios between aldehyde and ketone in the homogeneous phase experiments were 0.55 for 1,3-butanediol and 1.2 for 1,4-pentanediol.

Some experiments have been carried out in order to investigate the photocatalytic activity of silica bound W$_{10}$O$_{32}^{4-}$ under prolonged irradiation. Si-alkylNH$_3$W in CH$_2$Cl$_2$ has been chosen for the photooxidation of 1,4-pentanediol, since the data of Table 1 indicate that this photocatalyst presents the highest selectivity toward 4-hydroxypentanal. Fig. 1A shows that the aldehyde **2a**, including also its cyclic isomers **2c**, increased quite linearly during the photocatalytic experiment and represented the main product also after three hours irradiation, when about 50% of the initial diol underwent oxidation. Table 1 indicates that the most selective photocatalyst for the oxidation of 1,3-butanediol is Si-(alkyl)$_4$NW. Fig. 1B shows that its main product during the entire photocatalytic experiment was the ketone **1b**, whose concentration increased quite linearly vs irradiation time. It is noteworthy that after 225 min irradiation CO$_2$

was not formed in detectable amounts neither for 1,3-butanediol or 1,4-pentanediol. These findings are particularly relevant since it is quite difficult to stop the oxidation of an alcohol at the stage of aldehydes, which are known to be important building blocks in applied organic synthesis.

During prolonged irradiations, both Si-(alkyl)$_4$NW and Si-alkylNH$_3$W became light blue coloured, indicating that their reduced forms were accumulated in some amounts on silica support. In order to evaluate the amount of reduced decatungstate formed during irradiation, the powdered photocatalysts were analysed by titration with KMnO$_4$ at the end of the photocatalytic experiments. On the basis of this analysis, we concluded that the amount of reduced decatungstate formed during irradiation was about 2.5% of the total decatungstate, a negligible quantity that did not affect significantly the photocatalytic efficiency of decatungstate.

4. Conclusions

Heterogenization of W$_{10}$O$_{32}^{4-}$ on silica gel by chemical bond gives a robust photocatalyst for the selective oxidation of diols by O$_2$ upon near UV light and under mild pressure and temperature conditions. The polarity of the environment surrounding the photoactive anion plays a crucial role in controlling the adsorption of diols on the surface and, consequently, their reaction with the photoexcited decatungstate. We also conclude that site selective adsorption, a basic requirement to obtain high regioselectivity, can be fostered through a correct choice of the dispersing medium. The described reactions are a new appealing synthetic route for the selective oxidation of diols since proper reaction conditions have been found for obtaining more than 90% of 4-hydroxy-2-butanone from 1,3-butanediol. The oxidation of 1,4-pentanediol yields 4-hydroxypentanal with good selectivity. This is a particularly relevant result since it is quite difficult to stop the oxidation of an alcohol at the aldehyde, which are known to be important building blocks in organic synthesis.

Acknowledgments

Supplementary material

Supplementary material associated with this article can be found, in the online version, at DOI: 10.1016/j.jcat.2007.11.008.

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