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# Photocatalytic properties of sodium decatungstate supported on sol-gel silica in the oxidation of glycerol

# Alessandra Molinari<sup>a,\*</sup>, Andrea Maldotti<sup>a,\*</sup>, Amra Bratovcic<sup>a</sup>, Giuliana Magnacca<sup>b</sup>

<sup>a</sup> Dipartimento di Chimica, Università di Ferrara, Via Luigi Borsari 46, 44123 Ferrara, Italy

<sup>b</sup> Dipartimento di Chimica IFM; NIS, Center of Excellence, Università di Torino, Via P. Giuria 7, 10125 Torino, Italy

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### ABSTRACT

Photoexcitation of  $Na_4W_{10}O_{32}$  dissolved in water produces a powerful oxidizing reagent that is able to form hydroxyl radicals from water. OH• radicals formation has been demonstrated by EPR spintrapping technique using DMPO as spin trap. The photooxidation of glycerol occurs through its reaction with OH• radicals and is characterized by low selectivity and partial degradation of the substrate to CO<sub>2</sub>. Entrapment of  $Na_4W_{10}O_{32}$  inside a silica matrix by a sol-gel procedure gives a new heterogeneous photocatalyst characterized by the presence of micropores (7 and 13 Å) and mesopores (30 Å). Interaction between polyoxoanion and protonated silanol groups are strong and prevent any kind of leaching. The solid support affects the selectivity of the O<sub>2</sub>-assisted photooxidation process of glycerol. In particular, silica surface enhances alcohol adsorption improving its local concentration, so favouring its reaction with photogenerated OH• radicals that leads to glyceraldehyde and dihydroxyacetone. At the same time, carbon dioxide is not formed, thus indicating that it is possible to control the high oxidizing power of sodium decatungstate through its heterogenization on a suitable support.

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# 1. Introduction

Photocatalysis with polyoxotungstates for oxidation reactions continues to be a topic of intense research. It moves toward a "sustainable chemistry" opening to new oxidative routes that require  $O_2$  as available and cheap oxidant, mild temperature and pressure conditions and use of light as a renewable source of energy [1–3]. The decatungstate anion  $W_{10}O_{32}^{4-}$  has been intensively studied as very attractive photocatalyst for the transformation of organic compounds. A peculiar property of  $W_{10}O_{32}^{4-}$  is that it presents an absorption spectrum in the near UV region ( $\lambda_{max}$  = 323 nm) that partially overlaps the UV solar emission spectrum, opening the possibility to carry out benign solar-photoassisted applications [2–9].

Considerable attention has been recently devoted to the heterogenization of  $W_{10}O_{32}^{4-}$  following several procedures [10–22]: impregnation of porous inorganic networks, incapsulation in silica matrices by sol–gel methods, immobilization by ionic exchange, and occlusion in polymeric membranes. Main features of these photoactive materials are that they are easily handled and recyclable and that they can be employed in reaction media where they are insoluble. Moreover, it has been well established that heterogenization represents a suitable means to tailor efficiency and selectivity of photocatalytic processes through the control of the microscopic environment surrounding the photoactive polyoxoanion. More specifically, high specific surface area, typical of micro and mesoporous materials, and the appropriate ratio of surface hydrophobic/hydrophilic character are benefits for improving efficiency and selectivity of the process, the latter favouring the enrichment of substrates in the proximity of the photoactive polyoxotungstate.

We reported recently about the entrapment of  $(nBu_4N)_4W_{10}O_{32}$ in a silica matrix by a sol-gel procedure and demonstrated that the solid support has a strong effect on the oxygen-assisted photooxidation of 1-pentanol and 3-pentanol in organic solvent [22]. In the present work, we follow an analogous procedure to entrap Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> in a silica matrix. Detailed results on the characterization of this material are presented. Our attention is focussed on the photoreactivity of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> and on the possible effects of its heterogenization. The photocatalytic activity of the material is assessed in the photooxidation of glycerol in aqueous medium. This choice is ascribed to the fact that the extensive functionalization of this alcohol with similarly reactive hydroxy groups renders its selective oxidation particularly difficult. As a consequence, any improvement in selectivity is a noticeable issue. Moreover, glycerol

<sup>\*</sup> Corresponding authors. Tel.: +39 0532455147; fax: +39 0532240709. *E-mail addresses:* alessandra.molinari@unife.it (A. Molinari), andrea.maldotti@unife.it, mla@unife.it (A. Maldotti).

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is the primary by-product in biodiesel production and it is rapidly becoming a waste product with a related disposal cost. Thus, the development of new processes able to take advantage of this largely available and cheap molecule is a urgent need. Research is following different strategies to exploit glycerol: (i) its selective conversion into oxygenated derivatives that are higher value products [23,24], (ii) its use, in deaerated conditions, as sacrificial molecule in reforming [25–27] and photo-reforming processes [28–30] for H<sub>2</sub> production.

Up to now, only TiO<sub>2</sub> has been used for the photocatalytic oxidation of glycerol in aerated conditions [31,32]. A common issue is the need to control the high oxidation power of this photoexcited semiconductor, which may induce over-oxidation of the primary products up to carbon dioxide. Good selectivity to dihydroxyacetone and glyceraldehyde was obtained with surface fluorinated TiO<sub>2</sub> [31], while the use of rutile or anatase-rutile polymorphic phases did not prevent degradation of glycerol to CO<sub>2</sub> [32]. In this respect, heterogenized  $Na_4W_{10}O_{32}$  has been evaluated to be a valid alternative to titania systems.

# 2. Experimental

#### 2.1. Photocatalyst preparation and characterization

Reagents and solvents were purchased in the highest purities available from Sigma and used without further purification. Sodium decatungstate (Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>) was prepared following a literature procedure [33]. The heterogeneous photocatalyst  $(Na_4W_{10}O_{32}/SiO_2)$  was prepared by hydrolysis of tetraethylorthosilicate (TEOS) in the presence of an acid aqueous solution of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>, following a procedure recently published in detail for the entrapment of (nBu<sub>4</sub>N)<sub>4</sub>W<sub>10</sub>O<sub>32</sub> in silica [22]. On the basis of the solid mass obtained at the end of the preparation and the initial amount of  $Na_4W_{10}O_{32}$  employed (0.5 g), we could estimate that the prepared material Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/SiO<sub>2</sub> contained 30% (w/w) of decatungstate. The photocatalyst was washed several times with aliquots of water. UV-vis spectra of these aliquots showed that the release of  $Na_4W_{10}O_{32}$  into the solution was negligible. A sample not including decatungstate (SiO<sub>2</sub>) was also prepared, following the procedure described above but without adding  $Na_4W_{10}O_{32}$ .

Diffuse reflectance UV–vis spectra were recorded with a Jasco V-570 using an integrating sphere and BaSO<sub>4</sub> as reference. The plotted spectra were obtained by the Kubelka–Munk transformation  $(F(R) = 1 - R^2/2R)$  versus the wavelength. N<sub>2</sub> adsorption–desorption experiments were carried out at 77 K by means of ASAP2020 instrument (Micromeritics). Before each measurement, the sample was outgassed overnight at 150 °C with a rotative pump (residual pressure about  $10^{-2}$  mbar).

#### 2.2. EPR spin-trapping experiments

EPR spin-trapping experiments were carried out with a Bruker 220 SE spectrometer equipped with a TE 201 resonator, at a microwave frequency of 9.4 GHz. The samples for epr spin-trapping experiments were H<sub>2</sub>O/CH<sub>3</sub>CN (85/15) solutions containing 5,5-dimethylpyrroline *N*-oxide (DMPO,  $3 \times 10^{-2}$  M) as spin trap, Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> (2.4 × 10<sup>-3</sup> M) and, when requested, glycerol (1 × 10<sup>-2</sup> M). CH<sub>3</sub>CN was necessary in order to dissolve the spin trap. In heterogeneous experiments, the solid Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/SiO<sub>2</sub> was suspended in the solution containing DMPO and, when necessary, glycerol as described above. Then, samples were put into a flat quartz cell and directly irradiated into the EPR cavity at  $\lambda > 290$  nm with a Hg medium pressure mercury lamp. No EPR signals were obtained in the dark and during irradiation of the solution in the absence of photocatalyst.

#### 2.3. Photocatalytic experiments

Photocatalytic experiments were carried out inside a closed Pyrex tube of 15 mL capacity at  $298 \pm 1$  K. The desired amount of photocatalyst  $(4 \times 10^{-4} \text{ M} \text{ in the case of } Na_4 W_{10}O_{32}$  solution or 8 g/L in the case of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/SiO<sub>2</sub> suspension) was placed in 3 mL of an aqueous solution containing glycerol  $(1 \times 10^{-2} \text{ M})$ , and magnetically stirred for 20 min. The pyrex photoreactor was filled with  $O_2$  and then joined through an inlet tube to a balloon filled with  $O_2$ . Photochemical excitation (120 min) was performed by an external Helios Q400 Italquartz medium-pressure Hg lamp, selecting wavelengths higher than 290 nm with a cut off filter. The photon flux, measured with a MACAMUV203X ultraviolet radiometer, was 15 mW cm<sup>-2</sup>. At the end of the photocatalytic experiment, the sample was analyzed by HPLC system equipped with a photodiode array detector. The column used was an Alltech IOA-1000 Organic Acids,  $300 \times 7.8$  cm by GRACE. Double distilled water was used as eluent, filtered before use by a vacuum filtration system equipped with Whatman Nylon Membrane Filters 0.2 µm. The detected products were glyceraldehyde, dihydroxyacetone, glyceric acid. Quantitative analyses were carried out by calibration curves with commercial products. Each photocatalytic experiment was repeated three times in order to evaluate the errors, which never exceeded  $\pm 5\%$ . Control experiments were run irradiating SiO<sub>2</sub> suspended in the solution containing glycerol  $(1 \times 10^{-2} \text{ M})$ or keeping (120 min) the photocatalyst dispersed in the solution in the dark. When Na4W10O32/SiO2 was employed as a photocatalyst, the possible release of polyoxoanion in the solution phase was evaluated by UV-vis analysis of the solution at the end of irradiation.

In order to establish the amount of  $CO_2$  eventually formed, samples were irradiated maintaining the reactor firmly closed. At the end of irradiation 1.5 ml of a NaOH solution (0.1 M) were put inside the reactor with a syringe and mixed with the irradiated solution. Then, 3.5 mL of the aqueous solution were taken and kept into a vial. After the addition of 1 mL of saturated citric acid solution, carbon dioxide released was measured by pH meter BasiC 20 CRISON equipped with the gas sensing probe (Crison 9666). Quantitative analysis was made through a calibration curve built from standard solutions of NaHCO<sub>3</sub> treated as described above. Results obtained from the irradiated samples were compared with those coming from analogous samples kept in the dark for the same period. The yield of  $CO_2$  was referred to the number of carbon atoms present in the alcohol molecule.

#### 3. Results and discussion

#### 3.1. Textural characterization

Fig. 1a shows the UV-vis spectrum of heterogeneous  $Na_4W_{10}O_{32}/SiO_2$  (curve A). Spectra of homogeneous  $Na_4W_{10}O_{32}$ and of silica, obtained with the sol-gel procedure, are also reported for a comparison (curves B and C, respectively). It is seen that Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/SiO<sub>2</sub> presents an intense absorption at wavelengths lower than 400 nm that is typical of  $W_{10}O_{32}^{4-}$  and that is not present in the silica matrix. Fig. 1b reports the visible spectrum of  $Na_4W_{10}O_{32}/SiO_2$  irradiated in the presence of glycerol under anaerobic conditions (curve A). It is observed an important increase of absorption above 600 nm, in the region where the blue W<sub>10</sub>O<sub>32</sub><sup>5-</sup> typically absorbs (see for comparison curve C relative to homogeneous reduced decatungstate). Exposure to air of the irradiated powder leads to the reoxidation of decatungstate in its oxidized state that not absorbs in the visible region (curve B). These results are in line with the known primary photochemical process of decatungstate anion [4] and represent a further evidence that the polyoxoanion is unchanged in nature after its heterogenization



Fig. 1. (a) UV-vis spectra of  $Na_4W_{10}O_{32}/SiO_2$  (curve A), of homogeneous  $Na_4W_{10}O_{32}$  (curve B) and of SiO<sub>2</sub> (curve C). (b) Visible spectra of reduced  $Na_4W_{10}O_{32}/SiO_2$  (curve A), of oxidized  $Na_4W_{10}O_{32}/SiO_2$  (curve B) and of reduced homogeneous  $Na_4W_{10}O_{32}$  (curve C).

Gas-volumetric adsorption of N<sub>2</sub> at 77 K gives useful information about the morphological features of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/SiO<sub>2</sub> in comparison with SiO<sub>2</sub>. Table 1 reports that the introduction of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> into the silica matrix causes a decrease in surface specific area value. At the same time it is observed a 35% increase in the total pore volume.

 $Na_4W_{10}O_{32}/SiO_2$  material presents both mesoporosity and microporosity (Table 1). To evaluate both and, in particular, to reveal the porosity eventually present at the boundary between micro and mesoporosity regions, we employ here the same method recently adopted by us for the investigation of  $(n-Bu_4N)_4W_{10}O_{32}$ encapsulated inside a silica matrix [22] that consists in the isotherm deconvolutions in accordance to density functional theory (DFT) [34]. The pore volumes reported in Table 1 and Fig. 2 are classified on the basis of the pore size distribution determined via the DFT method and quantified considering the DFT cumulative pore volume curves.

Table 1	
Morphological features of $Na_4W_{10}O_{32}/SiO_2$ .	

Fig. 2 shows the incremental pore volume as a function of the pore width obtained via the DFT method that allows us to recognize the fraction of pores with widths between 10 and 20 Å.  $Na_4W_{10}O_{32}/SiO_2$  is characterized by micropores with width of about 7 Å, in agreement with the previous literature data on the entrapment of polyoxometalates in silica matrices via sol-gel techniques [18]. In addition to these micropores,  $Na_4W_{10}O_{32}/SiO_2$  also contains micropores around 13 Å and mesopores around 30 Å.

Table 1 and Fig. 2 show that the morphological features of  $Na_4W_{10}O_{32}/SiO_2$  differ markedly from those of its parent material SiO<sub>2</sub>. In fact, SiO<sub>2</sub> does not present 7Å micropores, but 75% of its porosity is characterized by micropores with width of 11–12Å. Moreover, the degree of mesoporosity is lower than in  $Na_4W_{10}O_{32}/SiO_2$ . These results indicate that the incorporation of sodium decatungstate during the synthesis of the silica-based photocatalyst induces an important modification of the porous texture of the siliceous material, suggesting that sodium decatungstate can act as a templating agent.

It has been reported in previous works that the formation of microporous decatungstate is due to the chemical interaction between sodium decatungstate and the silica network [18]. Since during the preparation the hydrolysis of TEOS in the presence of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> is carried out at pH 2, the silanol group ( $\equiv$ Si–OH) is protonated in the acidic medium to form  $\equiv$ Si–OH<sub>2</sub><sup>+</sup>. This can, in turn, act as a counterion for W<sub>10</sub>O<sub>32</sub><sup>4–</sup> yielding the couple ( $\equiv$ Si–OH<sub>2</sub><sup>+</sup>)(Na<sub>3</sub>W<sub>10</sub>O<sub>32</sub><sup>-</sup>)by acid–base reaction. This strong interaction could explain why the salt is no longer released although Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/SiO<sub>2</sub> is dispersed in aqueous media. It is noteworthy to evidence that the substitution of Na<sup>+</sup> ions with organic and less polar groups such as tetrabutylammonium ions [22] decreases the strength of the interaction between W<sub>10</sub>O<sub>32</sub><sup>4–</sup> and SiO<sub>2</sub> matrix, as observed in the effect induced by CH<sub>3</sub>CN washing of the material (loss of 20% of the starting decatungstate amount).

#### 3.2. EPR spin-trapping investigation

EPR spin-trapping investigation is a powerful technique for detecting the formation of short-lived radicals [35] and has been fruitfully employed in photochemical studies on polyoxometalates in order to better understand photochemical primary processes [36–41]. This technique is based on the ability of some molecules such as nitrones to trap radicals to give nitroxides stable enough to be successfully detected and studied. The nature of the trapped radical can be often identified by the parameters obtainable from the EPR spectrum.

Evidences of radical formation as a consequence of photoexcitation of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> in homogeneous solution have been obtained irradiating ( $\lambda > 290$  nm) H<sub>2</sub>O/CH<sub>3</sub>CN (85/15, v/v) solutions containing Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> (2.4 × 10<sup>-3</sup> M), glycerol (1 × 10<sup>-2</sup> M) and DMPO (3 × 10<sup>-2</sup> M) as a spin trap, directly inside the EPR cavity. Illumination causes the prompt formation of a quartet (1:2:2:1, a<sub>N</sub> = a<sub>H</sub> = 14.5 gauss), which is shown in Fig. 3. Signal pattern and coupling constant values are in agreement with the trapping of OH• radicals by DMPO to form the paramagnetic adduct [DMPO–OH]• according to step 2 of Scheme 1 [35]. No signals relative to the trapping of radicals coming from glycerol are detected even after some minutes irradiation. The same quartet is also obtained during irradiation of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> dissolved in an aqueous solution containing the spin trap but in the absence of glycerol, suggesting that the

Sample	$SSA/m^2g^{-1}$	$V_{\rm tot}/{\rm cm^3g^{-1}}$	$V_{ m micro}$ (<18 Å width, cm <sup>3</sup> g <sup>-1</sup> )	$V_{\rm meso}$ (>18 Å width, cm <sup>3</sup> g <sup>-1</sup> )
SiO <sub>2</sub>	772	0.176	0.131	0.045
Na <sub>4</sub> W <sub>10</sub> O <sub>32</sub> /SiO <sub>2</sub>	521	0.240	0.162	0.078



Fig. 2. DFT pore analysis for Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/SiO<sub>2</sub> (cross symbols) and for SiO<sub>2</sub> (solid line). The vertical broken line represents the threshold value considered (18 Å) between micro and mesopores.



**Fig. 3.** EPR spectrum of [DMPO–OH]• obtained upon irradiation ( $\lambda$  > 290 nm) of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> dissolved in an aqueous solution containing glycerol.



**Scheme 1.** Proposed reaction mechanism for glycerol oxidation by photoexcited  $Na_4W_{10}O_{32}$  in aqueous medium.

alcohol does not take part directly to the primary photoprocess. Control experiments show that no signal is observed neither in the dark nor during irradiation but in the absence of decatungstate.

The formation of OH• radicals may be ascribed to between photoexcited polyoxoanion reaction and water according to Scheme 1 (step 1). The possibility to obtain OH• radicals by direct reaction between photoexcited pentakis(isopropylammonium)hydrogenhexatungstate [NH<sub>3</sub>Pr<sup>i</sup>]<sub>5</sub>[W<sub>6</sub>O<sub>20</sub>(OH)] and water was pointed out by Yamase in the early eighties [42]. More recently, Papaconstantinou's group and other researchers proposed that polyoxometalates and TiO<sub>2</sub> exhibit overall similar photocatalytic behaviour in aqueous solution [1,5,43,44]. This similarity was attributed to the common formation of OH• radicals. In those works, the formation of OH• radicals was suggested by the detection of hydroxylation products in photocatalytic experiments with aromatic hydrocarbons, and on the basis of the excited state potentials [43].

The photogenerated OH• radicals can initiate glycerol oxidation by abstraction of a hydrogen atom from one of the available  $C_{\alpha}$  atoms, producing a hydroxy alkyl radical (step 3). Then, these radicals may be further oxidized to the corresponding carbonylic compounds (step 4). Reaction between reduced decatungstate and  $O_2$  regenerates the photocatalyst in its initial state (step 5). In our photocatalytic system, direct reaction of photoexcited  $W_{10}O_{32}^{4-}$ with the alcoholic substrate seems not to be the main pathway for glycerol oxidation since no radicals coming from the poly-alcohol are trapped by DMPO.

Fig. 4 shows that addition of glycerol causes a decrease of several times of the signal intensity of [DMPO–OH]<sup>•</sup>. This indicates that glycerol is a very good competitor for the reaction with OH<sup>•</sup> radical with respect to the spin trap (steps 2 and 3). It is also seen that the signal intensity of the paramagnetic [DMPO–OH]<sup>•</sup> adduct decreases rapidly after the first 120 s irradiation. Likely, this adduct can react with other radical species formed during irradiation (see for example step 5) or with the decatungstate itself, as reported in the past by some researchers [45].

It has been previously reported that the [DMPO-OH]• species may originate from degradation of the adduct [DMPO-OOH]• between DMPO and  $O_2^-$ . [46,47]. This paramagnetic species presents a typical 12-lines EPR spectrum [48]. On the other hand, this source of [DMPO-OH]• is expected to be negligible in our photocatalytic system on the basis of literature data indicating that a maximum level of approximately 3% [DMPO-OH]• should originate from [DMPO-OOH]• [46,49]. In line with this statement, Fig. 4 shows that the [DMPO-OH]• spectrum is the only observed



Fig. 4. Fixed-field EPR signal intensity of the [DMPO-OH]• adduct in time upon irradiation ( $\lambda$ > 290 nm) of a H<sub>2</sub>O/CH<sub>3</sub>CN solution (85/15, v/v) containing Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> (2.4 × 10<sup>-3</sup> M) and DMPO (3 × 10<sup>-2</sup> M) (squares) and of an analogous solution containing Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> (2.4 × 10<sup>-3</sup> M) and DMPO (3 × 10<sup>-2</sup> M) and glycerol (1 × 10<sup>-2</sup> M) (circles).

already after few seconds irradiation and that the presence of a scavenger of OH• radicals such as glycerol reduces significantly its intensity.

Analogous EPR spin-trapping experiments with heterogeneous  $Na_4W_{10}O_{32}/SiO_2$  were carried out suspending the photocatalyst in the solution containing DMPO and glycerol, when necessary. Results obtained are qualitatively similar to those in homogeneous phase: the unique signal observed is the quartet relative to the formation of [DMPO-OH]•, and in the presence of glycerol a severe decrease of intensity is observed again (Fig. 5). This indicates that the mechanism proposed in homogeneous phase is still working when decatungstate is entrapped inside the silica matrix. Intensities of signal obtained upon irradiation of  $Na_4W_{10}O_{32}/SiO_2$  are significantly lower than those observed in homogeneous conditions. This result can be tentatively ascribed to the fact that adsorption phenomena of glycerol on silica are expected to enhance



**Fig. 5.** Fixed-field EPR signal intensity of the [DMPO-OH]• adduct in time upon irradiation ( $\lambda$  > 290 nm) of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/SiO<sub>2</sub> dispersed in a H<sub>2</sub>O/CH<sub>3</sub>CN solution (85/15, v/v) containing DMPO (3 × 10<sup>-2</sup> M) (squares) and in an analogous solution containing also glycerol (1 × 10<sup>-2</sup> M) (circles).

its local concentration in proximity of the decatungstate, so favouring its reaction with the photogenerated OH• (Scheme 1, step 3) in competition with trapping by DMPO (step 2).

Adsorption of alcohols and diols on various siliceous matrices is an efficient phenomenon that has been already pointed out [12,14,50]. For this reason, glycerol is expected to adsorb on Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/SiO<sub>2</sub> too. A qualitative confirmation of this behaviour is obtained by the experiment described in the following: a huge amount of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/SiO<sub>2</sub> (70 g/L) was suspended in a small volume (0.7 mL) of the aqueous solution containing glycerol ( $1 \times 10^{-2}$  M) and stirred in the dark for 30 min. From HPLC analysis of the solution, performed before and after the contact with the photocatalyst, we observed a decrease of about 35% of the initial amount of glycerol, indicating that it can adsorb and concentrate on the surface.

#### 3.3. Photocatalytic activity

Typical photocatalytic experiments were carried out irradiating  $(\lambda > 290 \text{ nm}) \text{Na}_4 W_{10} \text{O}_{32} (4 \times 10^{-4} \text{ M}) \text{ or Na}_4 W_{10} \text{O}_{32}/\text{SiO}_2 (8 \text{ g/L}) \text{ in aqueous solutions containing glycerol } (1 \times 10^{-2} \text{ M}) \text{ at room temperature and under 760 Torr of O}_2$ . Owing to the presence of three oxidizable hydroxyl groups, a broad range of glycerol derivatives can be formed. Among them, we decided to follow by HPLC the formation of the carbonylic compounds, glyceraldehyde (GAD) and dihydroxyacetone (DHA), and of glyceric acid (GA), the less oxidized among acids that is obtained from further oxidation of the aldehyde. Moreover, CO<sub>2</sub> has been evaluated as final degradation product.

Irradiation of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> in homogeneous solution leads to the formation of GAD and DHA as primary oxidized products (Table 2). They represent about 75% of all the monitored compounds. According to EPR spin-trapping evidences, the formation of GAD and DHA should occur through steps 3 and 4 of Scheme 1. The subsequent easy oxidation of GAD may lead to the corresponding carboxylic acid. In fact, GA is about 10% of the converted glycerol.

This photocatalytic system shows quite strong oxidizing ability that it is difficult to control for synthetic purposes. In fact, the total yield to the primary photoproducts GAD, DHA and GA is only the 47% of the converted glycerol, which, likely undergoes overoxidation to yield a mixture of undetected  $C_3$  and  $C_2$  oxidized products, such as mesoxalic, tartronic, oxalic and glycolic acids. This statement is confirmed by the data of Table 2, which show that the photocatalytic experiment leads also to the formation of significant amounts of carbon dioxide.

These results are in line with EPR spin-trapping findings that demonstrate the formation of OH• radicals, which are very strong and unselective oxidants able to degrade both the initial substrate and the reaction intermediates. This photocatalytic behaviour of  $Na_4W_{10}O_{32}$  is also in agreement to what claimed by Papaconstantinou's group, who attributed the photocatalytic reactivity of polyoxotungstate anions toward phenols and 2-propanol in water to the formation of OH• radicals [43].

#### Table 2

Photocatalytic oxidation of glycerol by  $Na_4W_{10}O_{32}$  and  $Na_4W_{10}O_{32}/SiO_2$ .<sup>a</sup>

Photocatalytic system	Converted glycerol (µmol)	Detected products µmol (selectivity %) <sup>b</sup>			
		GAD	DHA	GA	CO <sub>2</sub> <sup>c</sup>
Na4W10O32 Na4W10O32/SiO2	19.2 9.6	6.3(32.8) 5.7(59.4)	0.54 (2.8) 0.54 (5.6)	1.8 (9.4) 0.51 (5.3)	0.45 (2.3) < 0.03 (0.3)

<sup>a</sup> In a typical experiment Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> ( $4 \times 10^{-4}$  M) or Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/SiO<sub>2</sub> (8 g/L) were put in aqueous solutions (3 mL) containing glycerol ( $1 \times 10^{-2}$  M) and irradiated (120 min) at  $\lambda > 290$  nm at 298 ± 1 K and 760 Torr of O<sub>2</sub>. Reported values are the mean of three repeated experiments.

<sup>b</sup> Selectivity % is expressed as µmol of product divided by µmol of converted glycerol. The remaining to 100% is represented by other oxidized derivatives that have not been identified.

<sup>c</sup> In order to compare directly the values of carbon dioxide with those of GAD, DHA and GA, the µmol of CO<sub>2</sub> have been divided by three.

Photocatalytic properties of  $Na_4W_{10}O_{32}$  in the oxidation of glycerol change significantly after its entrapment inside the silica matrix. Typical experiments were carried out irradiating the photocatalyst (8 g/L) suspended in an aqueous solution containing the alcohol. The amount of 8 g/L was chosen on the basis of measurements with an ultraviolet radiometer that indicate that photocatalyst absorbs 90% of the impinging radiation at 313 nm, which is the emission line of the employed light source closest to the absorption maximum of decatungstate at 323 nm. Control experiments give evidences that (i) irradiation of a dispersion of SiO<sub>2</sub> does not lead to the formation of detectable amounts of oxidation products, allowing us to exclude any kind of photoactivation of the silica matrix; (ii) no oxidation of glycerol occurs after the contact between the heterogenized decatungstate and the alcohol in the absence of light. Moreover, UV-vis spectra of solutions recovered after the irradiation of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/SiO<sub>2</sub> show that decatungstate is not released from the support. Further irradiation of these solutions does not accumulate extra oxidation products, thus indicating that the photocatalytic process is truly heterogeneous in nature.

Irradiation of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/SiO<sub>2</sub> leads mainly to the accumulation of GAD and DHA. In fact, they represent more than 90% of the monitored products. Further oxidation of GAD–GA occurs only in low degree, since the amount of acid accumulated during the photocatalytic experiment is four times lesser than that formed in the homogeneous sample. Moreover, the sum of GAD, DHA and GA is about the 70% of the converted glycerol and only a negligible amount of carbon dioxide is detected. All these findings indicate that heterogenization has an important effect in decreasing the oxidizing ability of sodium decatungstate.

The EPR spin-trapping investigation described above indicates that heterogenization does not affect the ability of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> to oxidize water to hydroxyl radicals (Scheme 1, step 1). Therefore, it should be not surprising that differences in selectivity can critically depend on textural features that allow the tuning of photocatalytic properties of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> through the control of surface interactions with substrates and intermediates [40,43,44]. In particular, EPR spin-trapping experiments give the indication that the reaction between OH• radical and glycerol occurs efficiently also in the heterogeneous system (Fig. 5). In agreement with this result, it is found that photocatalytic efficiency undergoes a decrease of only 25% after heterogenization. Likely, as mentioned above, adsorption phenomena of glycerol on silica enhance its local concentration in proximity of decatungstate. This substrate accumulation on the surface can favour, on the one hand, the reaction between glycerol and the photogenerated OH• radical and, on the other hand, can prevent the subsequent oxidation of the formed carbonylic compounds.

#### 4. Conclusions

Photoexcitation of  $Na_4W_{10}O_{32}$  dissolved in water produces a powerful oxidizing reagent. The oxidizing ability is manifested through formation of hydroxyl radicals arising from the reaction of excited  $Na_4W_{10}O_{32}$  and water. OH• radical formation has been demonstrated by EPR spin-trapping technique using DMPO as spin trap. Photoexcited homogeneous  $Na_4W_{10}O_{32}$  is an efficient catalyst for the oxidation of glycerol but, since its photocatalytic activity depends on OH• radicals, it shows low selectivity and leads to over oxidation and complete degradation of the substrate.

Entrapment of  $Na_4W_{10}O_{32}$  inside a silica matrix by a sol-gel procedure gives a heterogeneous photocatalyst characterized by the presence of micropores of about 7 Å and 13 Å and mesopores of about 30 Å. The morphological features of  $Na_4W_{10}O_{32}/SiO_2$  differ from those of SiO<sub>2</sub> prepared following the same procedure,

indicating that incorporation of decatungstate induces an important modification of the porous texture of the siliceous material. Interactions between polyoxoanion and protonated silanol groups are strong and the photocatalyst is never released from the solid matrix.

The photochemical characterization of  $Na_4W_{10}O_{32}/SiO_2$  in the  $O_2$ -assisted oxidation of glycerol shows that the solid support has a strong effect on the selectivity. In particular, silica surface favours adsorption of glycerol, enhancing its local concentration. This facilitates its reaction with OH• radicals photogenerated by decatungstate placed on the surface or inside pores. As a consequence, a significative improvement in selectivity toward primary oxidation compounds is obtained with negligible amounts of carbon dioxide. The results reported in this study provide new insights into the role of textural features in tuning the photocatalytic properties of  $Na_4W_{10}O_{32}$ . Comprehension of the morphology and of surface properties can represent the starting point for developing selective photocatalytic systems, an issue of particular relevance when the oxidizable substrates present large functionalization with groups of similar reactivity.

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