Heterogeneous photocatalysis for synthetic purposes: oxygenation of cyclohexane with $H_3PW_{12}O_{40}$ and $(nBu_4N)_4W_{10}O_{32}$ supported on silica

Alessandra Molinari, Rossanno Amadelli, Leonardo Andreotti and Andrea Maldotti*

Dipartimento di Chimica, Centro di Studio su Fotoreattività e Catalisi del C.N.R., Università degli Studi di Ferrara, Via L. Borsari 46, 44100, Ferrara, Italy. E-mail: mla@dns.unife.it

Heterogenisation of $H_3PW_{12}O_{40}$ and $(nBu_4N)_4W_{10}O_{32}$ with silica provides new photocatalytic systems able to oxygenate cyclohexane with O_2 without causing the oxidative mineralization processes which typically occur on the surface of the photosensitive semiconductor TiO_2.

Catalytic oxidation of unactivated C–H bonds under mild conditions (room temperature and atmospheric pressure), using environmentally friendly reagents such as O_2, is a field of ever growing interest.[1] In this context, a number of authors are investigating photoexcited polyoxometalates, which exhibit a noticeable activity in the oxidation of numerous organic compounds, including saturated hydrocarbons.[2] Some of our recent contributions in this research area deal with the oxygenation of alkanes photocatalysed by $(nBu_4N)_4W_{10}O_{32}$ and by $H_3PW_{12}O_{40}$ in homogeneous solution.[3]

In view of the interest in the heterogenisation of polyoxometalates,[4] the photocatalytic activity for cyclohexane oxidation of the two mentioned polyoxotungstates supported on silica is here reported for the first time. We demonstrate that both supported polyoxotungstates present the important advantage of being more easily handled than in the homogeneous phase. An important aspect is that their photocatalytic activity can be investigated in media where they are insoluble. Specifically, we could investigate both of them in pure cyclohexane and observe a quite good selectivity for the ketone formation in the case of $H_3PW_{12}O_{40}/SiO_2$. Since we describe heterogeneous photosensible systems, the comparison with a dispersed semiconductor such as TiO_2 becomes natural. Contrary to this well investigated semiconductor,[5] the $(nBu_4N)_4$-$W_{10}O_{32}/SiO_2$ photocatalyst does not cause any mineralisation of the substrate, while maintaining a comparable efficiency for the reaction under investigation.

$H_3PW_{12}O_{40}$ was heterogenised on silica following the previously described † 'impregnation' procedure which results in the fixation of the polyoxoanion to the support, possibly through electrostatic interactions with the protonated silica surface.[6] We successfully applied the same method to support $(nBu_4N)_4W_{10}O_{32}$.† Since this compound is present in the form of cation–anion aggregates in organic solvent,[7] it is likely that it is adsorbed on silica as an ionic couple, with the tetraalkylammonium cations acting as a bridge between the surface and the decatungstate anion. This interpretation is supported by previous investigations on the modes of polyoxomolybdate adsorption on silica,[8] as well as by infrared spectra, which reveal the presence of $(nBu_4N)^+$ cations and $W_{10}O_{32}{}^{4-}$ on the surface of the support.‡

Table 1 reports the photocatalytic properties of the so obtained heterogeneous systems in the oxygenation of cyclohexane at 20 °C and 760 Torr of O_2, in different dispersing media and at excitation wavelengths chosen on the basis of the absorption spectra of the two polyoxotungstates§ (entries 1,2,6,7). Table 1 also shows some data previously obtained in homogeneous solution (entries 3 and 8), where the cyclohexane photooxidation quantum yields are 0.35 at 325 nm and 0.03 at 254 nm for $(nBu_4N)_4W_{10}O_{32}$ and $H_3PW_{12}O_{40}$, respectively.[3] Finally, entries 4 and 5 report the results obtained using TiO_2 powder dispersions to induce cyclohexane photooxidation, according to previously reported investigations.[9]

Table 1 Photocatalytic oxidation of cyclohexane by O_2 (760 Torr)

Entry	Photocatalytic system	Solvent or dispersing medium	Excitation wavelengths/ nm (irradiation time/min)	Product ratio[a] cyclohexanone: cyclohexanol	CO_2[a]/ μmol	Alcohol + ketone/ μmol
1[b]	$(nBu_4N)_4W_{10}O_{32}/SiO_2$	C_6H_{12}	$\lambda > 280$ (90)	1	<0.5	22
2[b]	$(nBu_4N)_4W_{10}O_{32}/SiO_2$	C_6H_{12}/CH_2Cl_2 1/1	$\lambda > 280$ (90)	1	<0.5	36
3[c]	$(nBu_4N)_4W_{10}O_{32}$[3]	$CH_2Cl_2/C_6H_{12}/CH_3CN$ 6/3/1	$\lambda > 280$ (90)	1	<0.5	25
4[d]	TiO_2[9]	C_6H_{12}	$\lambda > 280$ (90)	5.7	3	23
5[d]	TiO_2[9]	C_6H_{12}/CH_2Cl_2 1/1	$\lambda > 280$ (90)	1.5	5	42
6[b]	$H_3PW_{12}O_{40}/SiO_2$	C_6H_{12}	$\lambda = 254$ (360)	2.3	<0.5	4
7[b]	$H_3PW_{12}O_{40}/SiO_2$	C_6H_{12}/CH_2Cl_2 1/1	$\lambda = 254$ (360)	1.1	<0.5	4
8[c]	$H_3PW_{12}O_{40}$[3]	$CH_2Cl_2/C_6H_{12}/CH_3CN$ 6/3/1	$\lambda = 254$ (360)	1	<0.5	6

[a] Analysis of cyclohexanol and cyclohexanone was carried out by gas chromatography and carbon dioxide was determined by a turbidimetric method using an absorbing solution of $Ba(OH)_2$ in glycerol. Reported values are ±10%. [b] 3 ml of dispersing medium containing 15 g l^{-1} of supported polyoxotungstate. 1.45 μmol of irradiated polyoxotungstate. [c] 3 ml of solution 2×10^{-4} mol dm^{-3}. 0.6 μmol of irradiated polyoxotungstate. CH_3CN is necessary for the dissolution of the catalyst. [d] 3 ml of dispersing medium containing 3 g l^{-1} of TiO_2.

In every case, photoexcitation of the two polyoxotungstates leads to the oxidation of cyclohexane to cyclohexanol and cyclohexanone as the main stable products (more than 90% of the overall oxidised alkane). The ketone to alcohol concentration ratio is always close to one except in entry 6 where the $H_3PW_{12}O_{40}/SiO_2$ presents a good selectivity for the ketone formation. Iodometric analysis indicates that hydroperoxides, which are proposed to be the primary products during the oxygenation of alkanes by illuminated $(nBu_4N)_4W_{10}O_{32}$,[4,10] are present only in negligible amounts (less than 5% of the overall oxidized cyclohexane). As far as the stability of the photocatalysts is concerned, it is noteworthy that they can be used for subsequent cycles of oxidation without any release of the polyoxotungstates during the experiments, and without any loss of their photocatalytic activity.

It is to be noted that entries 1–5 in Table 1 allow a semiquantitative comparison of the photocatalytic properties of $(nBu_4N)_4$-$W_{10}O_{32}$, $(nBu_4N)_4W_{10}O_{32}/SiO_2$ and TiO_2 because (i) excitation wavelength range and irradiation time are the same; (ii) the amounts of the photocatalysts have been chosen so as the maximum absorption of the incident light is the same for all the systems (see notes *b*, *c* and *d* in Table 1). On this basis, we can state that heterogenisation of $(nBu_4N)_4W_{10}O_{32}$ inhibits only partially its photocatalytic efficiency expressed as the ratio between the value of the μmoles of oxidized cyclohexane, reported in the last column of Table 1 (entries 2, 3), and the μmoles of irradiated decatungstates: 25 in the heterogeneous system and 41 μmol in the homogeneous one (see notes *b*, *c* and *d* in Table 1).

Despite a different product distribution, both in cyclohexane (entries 1, 4) and in mixed solvent (entries 2, 5), the μmoles of oxidised cyclohexane with $(nBu_4N)_4W_{10}O_{32}/SiO_2$ are very close to those obtained with TiO_2. Although a quantitative comparison between the two heterogeneous systems is difficult, it is reasonable to speculate that the photoactive centres on the heterogeneous polyoxotungstate catalyst are sensibly lower than for an equal amount of TiO_2. This makes the $(nBu_4N)_4$-$W_{10}O_{32}/SiO_2$ system even more interesting from an efficiency point of view. Another reason that makes the heterogenised decatungstate very promising for applied synthetic purposes is that, in contrast to TiO_2, it does not induce any mineralisation process of the substrate. In fact, it photocatalyses the oxygenation of cyclohexane to cyclohexanone and cyclohexanol without the formation of carbon dioxide.

Acknowledgements

Notes and references

† 0.1 g of catalyst $H_3PW_{12}O_{40}$ or $(nBu_4N)_4W_{10}O_{32}$ was dissolved in a suitable solvent (H_2O and CH_3CN, respectively) and then 1 g of colloidal silica (0.012 μm, Strem Chemicals) was added. After stirring and evaporation of the solvent, the obtained powder contained about 10% (w/w) of polyoxotungstate.

‡ Infrared spectra of $(nBu_4N)_4W_{10}O_{32}/SiO_2$ were recorded in KBr using a diffuse reflectance accessory. nBu_4N^+: stretching of $-CH_3$ and $-CH_2$ (2963 and 2875 cm^{-1}), and bending of C–H (1481 and 1383 cm^{-1}). $W_{10}O_{32}{}^{4-}$: 958, 890, 802 cm^{-1}.

§Irradiation of $(nBu_4N)_4W_{10}O_{32}/SiO_2$ and of TiO_2 was performed with a Hanau Q 400 Hg lamp, using a suitable cut-off filter ($\lambda > 280$ nm; 15 mW cm^{-2}), while $H_3PW_{12}O_{40}/SiO_2$ system was irradiated with a Hg low pressure lamp ($\lambda = 254$ nm; 3 mW cm^{-2}). All the experiments were carried out at 20 ± 1 °C under oxygen at 760 Torr.

1 A. Bielanski and J. Haber, *Oxygen in Catalysis*, Marcel Dekker, New York, Basel, Hong Kong, 1991; A. Kroty and J. P. Kingsley, *Chemtech*, 1996, 39.

2 M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer Verlag, Berlin, Heidelberg, New York, Tokyo, 1993; C. L. Hill and C. M. Prosser-McCartha, *Photosensitization and Photocatalysis using Inorganic and Organometallic Compounds*, Kluwer Academic Publishers, Dordrecht, 1993.

3 A. Maldotti, A. Molinari, P. Bergamini, R. Amadelli, P. Battioni and D. Mansuy, *J. Mol. Catal.*, 1996, **113**, 147; A. Maldotti, A. Molinari, R. Argazzi, R. Amadelli, P. Battioni and D. Mansuy, *J. Mol. Catal.*, 1996, **114**, 141; A. Maldotti, R. Amadelli, V. Carassiti and A. Molinari, *Inorg. Chim. Acta*, 1997, **256**, 309; A. Molinari, A. Maldotti, R. Amadelli, A. Sgobino and V. Carassiti, *Inorg. Chim. Acta*, 1998, **272**, 197.

4 N. Mizuno and M. Misono, *Chem. Rev.*, 1998, **98**, 199; L. K. Volkova, E. S. Rudakov and V. P. Tretyakov, *Kinet. Katal.*, 1996, **37**, 540; 1995, **36**, 373.

5 M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chem Rev.*, 1995, **95**, 69; P. Pichat, *Catal. Today*, 1994, **19**, 313.

6 Y. Wu, X. Ye, X. Yang, X. Wang, W. Chu and Y. Hu, *Ind. Eng. Chem. Res.*, 1996, **35**, 2546.

7 M. Fournier, R. Thouvenot and C. Rocchiccioli-Deltcheff, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 349.

8 C. Rocchiccioli-Deltcheff, M. Amirouche, M. Che, J. M. Tatibout and M. Fournier, *J. Catal.*, 1990, **125**, 292; A. Chemseddine, C. Sanchez, J. Livage, J. P. Launay and M. Fournier, *Inorg. Chem.*, 1984, **23**, 2609.

9 P. Boarini, V. Carassiti, A. Maldotti and R. Amadelli, *Langmuir*, 1998, **14**, 2080; R. Amadelli, M. Bregola, E. Polo, V. Carassiti and A. Maldotti, *J. Chem. Soc., Chem. Commun.*, 1992, 1355; W. Mu and J. M. Pichat, *Catal. Lett.*, 1989, **3**, 73.

10 L. P. Ermolenko and C. Giannotti, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1205; L. P. Ermolenko, J. A. Delaire and C. Giannotti, *J. Chem. Soc., Perkin Trans. 2*, 1997, 25.

Communication 9/01051C