

Photooxygenation of hydrocarbons over efficient and reusable decatungstate heterogenized on hydrophobically-modified mesoporous silica†

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Decatungstate $W_{10}O_{32}^{4-}$ heterogenized on a novel hydrophobically-organomodified SBA-15 was proven an efficient, green and reusable catalyst for photooxygenation by oxygen of a range of aryl alkanes to the corresponding ketones under mild conditions.

Direct conversion of hydrocarbons into highly desirable oxygenates is one of the most challenging reactions in synthetic chemistry.¹ Although a number of methods have been developed, the search for new facile, cost-effective, energy efficient and green procedures has attracted substantial interest.² An attractive alternative is the photocatalytic oxygenation with dioxygen or air as the sole terminal oxidant, which represents a key strategy towards the development of new sustainable methods for “greener” chemical synthesis.³ In particular, the development of soluble polyoxometalates (POMs) as efficient catalysts that can allow solar-photoassisted oxygenation of alkanes under mild conditions has attracted special attention.⁴ One distinct advantage of POMs is that a wide range of redox potentials can be readily attained,⁵ which enables a remarkable array of homogeneous oxidation reactions.^{4–7} Among them, decatungstate $W_{10}O_{32}^{4-}$ appears to be particularly suitable for the catalytic functionalization of inert C–H bonds owing to its powerful oxidizing capacity.⁷ From a practical point of view, however, it is more attractive to develop a solid and reusable photocatalyst that is efficient for this transformation.

Heterogenization of POMs has attracted tremendous recent attention by providing an easily adaptable technique for fabrication of new recoverable photocatalytic materials with well-defined and tailored molecular structure.^{8–11} So far, several technical procedures including simple impregnation of a solid carrier⁸ and immobilization with amino-functionalized amorphous silica⁹ have been developed to prepare heterogenized $W_{10}O_{32}^{4-}$ catalysts for various applications. Other methods like embedding in polymeric membranes¹⁰ or inside the silica network¹¹ have also been used. However, these methods have presented general problems which include

limited activity or stability during the reaction.¹² In view of the intrinsic hydrophilic nature of the mesoporous silica surface (the active sites in which may not be easily accessible to the hydrocarbon molecules), it is conceivable that introduction of additional hydrophobic organic fragments onto the silica surface may provide unique opportunity for fabricating new efficient heterogeneous $W_{10}O_{32}^{4-}$ system. Herein, we report for the first time heterogenization of $W_{10}O_{32}^{4-}$ on a novel hydrophobically-modified SBA-15, which was proven an efficient, green and reusable photocatalyst for oxygenation of a range of aryl alkanes under ambient conditions.

The organomodified SBA-15 was prepared by an initial insertion of alkyl groups *via* refluxing with C_n -Si(OEt)₃, followed by grafting 3-aminopropyl groups on to the parent support.¹³ The resultant material was denoted as C_n -AP-SBA, where C_n is the alkyl group (n is the number of the carbon atoms of the alkyl group) and AP is the 3-aminopropyl groups. A series of photocatalysts having different alkyl-chain length was prepared by acidification of C_n -AP-SBA using trifluoromethanesulfonic acid and ion exchange by decatungstate,¹⁴ denoted as W_{10}/C_n -AP-SBA (experimental details are shown in the ESI†). In this process, the 3-ammoniumpropyl groups, $-(CH_2)_3NH_3^+$, immobilize the $[W_{10}O_{32}]^{4-}$ polyanions on the pore walls while the alkyl groups form hydrophobic regions around the decatungstate. A decrease of the BET surface areas is observed after the post-grafted process; the BET surface areas of SBA-15, AP-SBA, C8-AP-SBA and W_{10}/C_8 -AP-SBA are 757, 613, 461 and 376 m² g⁻¹, respectively. Infrared spectra, UV-Vis spectra and ICP analysis confirmed that the molecular structure of the decatungstate anions was maintained in the catalysts (see ESI†). TEM, N₂ adsorption isotherms confirmed that the catalysts maintained the mesostructure of SBA-15 (see ESI). Elemental analysis of the heterogenized W_{10}/C_n -AP-SBA using ICP gave *ca.* 12 wt% loading of decatungstate.

To start our investigations, we examined the photooxygenation of ethylbenzene using dioxygen (O₂) as the oxidant at ambient temperature (see ESI for experimental details†). Several tungsten-based catalyst systems were investigated, including the homogeneous POM system (Table 1, entry 1), solid WO₃ (Table 1, entry 2), and the heterogenized decatungstate system with various surface modification (Table 1, entries 6–10). Of all catalysts tested, the octyl-grafted catalyst showed the highest reactivity (Table 1, entry 9). All other tested catalysts showed lower or no reactivity. It is interesting to note that the corresponding catalytic activities

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Table 1 Results on ethylbenzene photooxidation to acetophenone with O₂ over different catalysts in CH₃CN as solvent^a

Entry	Catalyst	S/C ^b	Conversion (mol%)	Selectivity (mol%)	TOF/h ⁻¹
1 ^c	(Bu ₄ N) ₄ W ₁₀ O ₃₂	300	44	64.4	22
2	WO ₃	300	1.6	96	0.8
3	AP-SBA	—	—	—	—
4 ^d	PW/AP-SBA	300	6.3	77.6	3.2
5 ^e	SiW/AP-SBA	300	4.7	83.6	2.4
6	W ₁₀ /AP-SBA	300	47	84	23.5
7	W ₁₀ /C ₂ -AP-SBA	300	49	88	24.5
8	W ₁₀ /C ₄ -AP-SBA	300	53	90	26.5
9	W ₁₀ /C ₈ -AP-SBA	300	60	90.1	30
10	W ₁₀ /C ₁₆ -AP-SBA	300	52	91	26

^a Reaction conditions: ethylbenzene = 1.7 mmol, 13 mL solvent, oxygen flow = 3 mL min⁻¹, reaction for 6 h. ^b S/C is the molar ratio of ethylbenzene to decatungstate. ^c (Bu₄N)₄W₁₀O₃₂ was dissolved in CH₃CN. Reported values are the mean of two repeated experiments and are ± 3%. ^d PW means PW₁₂O₄₀³⁻. ^e SiW means SiW₁₂O₄₀⁴⁻.

of the organomodified catalysts comprising ethyl, butyl, and octadecyl groups were all lower than those of the octyl-grafted catalyst. The reason for such alkyl length-dependence behavior is probably due to the similar dimension of the octyl groups relative to that of the decatungstate W₁₀O₃₂⁴⁻ species (*ca.* 1 nm), which can afford more suitable conditions for the highly active photooxygenation.¹⁵

Next, we investigated the influence of the solvent on the performance of W₁₀/C₈-AP-SBA in more detail (Table 2). Remarkably, an equal volume mixture of CH₃CN–H₂O (1:1 v/v) is revealed as the solvent of choice. Changing the solvent to dichloromethane and 1,2-dichloroethane lowered conversion of ethylbenzene to 40% and 46% (Table 2, entries 1 and 2), respectively. An even lower conversion was found when the solvent was changed to acetone or water (Table 2, entries 3 and 8). It is noted that about 9% of oxygenated product is hydroperoxides using pure CH₃CN as solvent after reaction for 6 h, which are found to be the

Table 2 Results of ethylbenzene photooxidation to acetophenone with O₂ over W₁₀/C₈-AP-SBA in various solvents^a

Entry	S/C	Solvent	Conversion (mol%)	Selectivity (mol%)	TOF/h ⁻¹
1	300	CH ₂ Cl ₂	40	74.8	20
2	300	ClCH ₂ CH ₂ Cl	46	69.7	23
3	300	CH ₃ COCH ₃	35	88.6	18
4	300	CH ₃ CN	60	90.1	30
5	300	CH ₃ CN–H ₂ O (3:1 v/v)	67	93.6	34
6	300	CH ₃ CN–H ₂ O (1:1 v/v)	87	96.5	44
7	300	CH ₃ CN–H ₂ O (1:3 v/v)	78	97.4	39
8	300	H ₂ O	8	87.5	4

^a Reaction conditions: ethylbenzene = 1.7 mmol, 13 mL solvent, oxygen flow = 3 mL min⁻¹, reaction for 6 h at 5–10 °C.

primary products during the oxygenation of alkanes by illuminated (Bu₄N)₄W₁₀O₃₂.¹⁶ While the reaction in pure water showed moderate selectivity toward ketone products (Table 2, entry 8), the use of cosolvent of CH₃CN–H₂O mixture can afford the formation of acetophenone with a high selectivity well above 90%. The ratio of water to acetonitrile was varied (Table 2, entries 5–7) which revealed that a 1:1 mixture provided the most active and selective catalyst. Presumably, appropriate amount of water can favour the decomposition of hydroperoxides to give the formation of acetophenone in the presence of W₁₀/C₈-AP-SBA under the photooxygenation reaction conditions.¹⁷

One important issue when working with heterogenized systems is the recyclability of the final material during the course of the reaction. The W₁₀/C₈-AP-SBA catalyst was stable and can be easily reused during reactions in CH₃CN–H₂O (1:1 v/v) mixture. After the first ethylbenzene oxidation, the catalyst was separated from the reaction mixture by filtration, thoroughly washed with acetone, and then reused as catalyst for the next run under the same conditions. As shown in Table 3, the acetophenone yields remained essentially constant for the five successive cycles, reflecting high stability and reusability of the catalyst. This is consistent with the characterization results for this catalyst. TEM (Fig. S2[†]) and IR (Fig. S3[†]) results show essentially no changes in the nanostructure of the SBA-15 support and decatungstate species, respectively, after the five successive runs. Moreover, it was confirmed by ICP that the W content of the used W₁₀/C₈-AP-SBA catalyst was the same as that of the fresh catalyst and that no W was in the filtrate.

To examine the scope of the photooxygenation reaction with the W₁₀/C₈-AP-SBA system, we extended our studies to various aryl alkanes. The results are summarized in Table 4. It was found that the photooxygenation of alkylbenzenes with varying alkyl chain length (C₂–C₄) all proceeded efficiently, giving the corresponding phenones as mainly products (Table 4, entries 1–3). The decreasing selectivity toward ketone products with increasing chain length is indicative of a preferential oxidation of the C–H bond at α -methylene group. It is especially noteworthy that W₁₀/C₈-AP-SBA was highly active and selective for the photooxygenation of ethylbenzene, with an almost exclusive formation of acetophenone corresponding to a turnover frequency (TOF) of *ca.* 47 h⁻¹ for chemoselective conversion of ethylbenzene can be achieved (Table 4, entry 1). In contrast, a previously reported decatungstate-based system is found to be moderately active for photoconversion of this substrate.¹⁸ Moreover, the W₁₀/C₈-AP-SBA showed high activity even when the reaction was carried out using air in place of O₂, although a longer reaction time is required (Table 4, entry 7).

Table 3 Photooxidation of ethylbenzene with O₂ catalyzed by W₁₀/C₈-AP-SBA^a

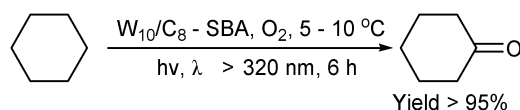
Reuse number	1	2	3	4	5
%Yield of acetophenone	85	84	83	83	83

^a Reaction conditions: ethylbenzene = 1.7 mmol, 13 mL CH₃CN–H₂O (1:1 v/v) as solvent, oxygen flow = 3 mL min⁻¹, reaction for 6 h at 5–10 °C.

Table 4 Results for the photooxidation of various alkanes catalyzed by W_{10}/C_8 -AP-SBA using dioxygen^a

Entry	Substrate	Reaction time/h	Conv. (mol%)	Major product (selectivity, mol%)
1	Ethylbenzene	7	97	Acetophenone (99)
2	Propylbenzene	8	81	Propiophenone (90.8)
3	Butylbenzene	6	44	Butyrophenone (50.5)
4	Cumene	8	87	Acetophenone (51), 1,1-dimethylbenzyl alcohol (47)
5	Diphenylmethane	12	78	Benzophenone (95.3)
6	Cyclohexyl-Benzene	6	28	3-Phenylcyclohexanone (64), 4-phenylcyclohexanone (25)
7 ^b	Ethylbenzene	7	89	Acetophenone (97)

^a Reaction conditions: S/C = 300, 13 mL CH_3CN-H_2O (v/v) = 1:1 as solvent, oxygen flow = 3 mL min^{-1} , temperature 5–10 °C. ^b Using air as oxidant.

**Scheme 1**

The selective and facile oxidation of cyclohexane to cyclohexanone is also a highly valuable transformation in organic synthesis for both laboratory and industrial manufacturing, since the oxygenated products of cyclohexane are important intermediates in the production of ϵ -caprolactam and adipic acid which are used in the manufacture of nylon-6 and nylon-66 polymers.¹⁹ The development of an efficient catalytic system to achieve this goal has attracted considerable effort recently.^{8,20} Given the excellent chemoselectivity of heterogenized $W_{10}O_{32}^{4-}$ for ethylbenzene oxygenation, it was decided to investigate whether W_{10}/C_8 -AP-SBA could provide a viable solution to this challenge. The result showed that W_{10}/C_8 -AP-SBA mediated photooxygenation can afford highly efficient photocatalytic oxidation of cyclohexane to cyclohexanone (Scheme 1). It is remarkable that 100% chemoselectivity in terms of cyclohexanone production can be achieved for cyclohexane conversion. Such reaction exclusivity, notably the absence of cyclohexanol and any other autooxidation products, is unique when compared with the conventional catalytic systems.^{8,20}

In conclusion, we have demonstrated that $W_{10}O_{32}^{4-}$ heterogenized on hydrophobically modified SBA-15 has great potential for photooxygenation of a range of aryl alkanes to corresponding ketones under mild conditions. This catalyst has been proven to be highly efficient and chemoselective in the photooxygenation of ethylbenzene and cyclohexane. The efficiency and stability of the catalyst has also been demonstrated convincingly by conducting six successive runs without appreciable drop in the reaction rate.

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