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Green photocatalytic organic transformations by polyoxometalates vs. mesoporous TiO₂ nanoparticles: selective aerobic oxidation of alcohols†

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In this study, the catalytic activity of decatungstate (W₁₀O₃₂⁴⁻) supported on mesoporous TiO₂ nanoparticle assemblies (DT-MTA) was compared with that of homogeneous [Bu₄N]₄W₁₀O₃₂ catalysts under mild conditions. Our experiments showed that both catalytic systems achieve exceptionally high activity and selectivity under UV-visible light oxidation of various *para*-substituted aryl alcohols, using molecular oxygen as a "green" oxidant. The chemoselective transformation of aryl alcohols into the corresponding ketones was investigated with gas chromatography (GC) and NMR spectroscopy. Product analysis and kinetic results also indicated that these photooxidation reactions proceed *via* both electron transfer (ET) and hydrogen atom transfer (HAT) mechanisms over the DT-MTA catalyst, with the former one as the predominant, whereas a HAT route was adopted to account for the decatungstate homogeneous catalyzed reactions.

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Introduction

For catalytic oxo-functionalization processes,¹ an attractive approach is the use of a solid, recyclable catalyst in the presence of environmentally friendly oxidants such as molecular oxygen.² The use of supported catalysts on well-ordered metal oxide surfaces offers several advantages over homogeneous systems, including catalyst recovery and controlled regio- and chemo-selective reactions.³ In addition, supported catalysts may exhibit larger catalytically active surface area and better accessibility of reactants to the active sites. So far, various photocatalytic reactions with metal oxide semiconductors such as TiO₂, ZnO, CeO₂, Fe₂O₃, CdS and WO₃ have been extensively studied.⁴ These include degradation of organic pollutants, oxidation of small organic molecules and photocatalytic splitting of water into hydrogen and oxygen.⁵

During the past few years, important advances have been made in the use of various polyoxometalate (POM) clusters supported on metal oxide surfaces as heterogeneous catalysts for the oxidation of organic substrates.^{6,7} Among them, decatungstate anion (W₁₀O₃₂⁴⁻) is one of the most prominent examples, which has been widely studied due to its excellent

chemical stability and interesting photocatalytic activity.⁸ Nevertheless, reports concerning the synthesis of heterogenized decatungstate catalysts are scarce and are mostly based on the stabilization of W₁₀O₃₂⁴⁻ anions on silica and zirconia mesoporous supports.^{8,9} These hybrid mesostructures have been successfully applied for the photooxidation of aliphatic alkanes, alkenes and alcohols.^{9–12}

In a previous work, we have shown that decatungstate clusters deposited on silica and γ -alumina surfaces, by wet impregnation at different pH values, catalyze the photooxidation of selected aromatic alcohols to the corresponding carbonyl products with high yields.¹³ Following our general interest on the homogeneous and heterogeneous catalytic oxidation of aromatic compounds, we report here the chemoselective oxidation of various *para*-alkyl substituted aryl alcohols by a decatungstate catalyst supported on high-surface-area mesoporous TiO₂ nanoparticle assemblies (DT-MTA).¹⁴ For comparison, the relevant oxidation reactions over the homogeneous [Bu₄N]₄W₁₀O₃₂ (TBADT) catalyst is also discussed. Finally, a proposed mechanistic pathway for the synthesis of oxidation products is also suggested.

Experimental

Synthesis of the DT-MTA catalyst

Mesoporous sensitized TiO₂ nanoparticle assemblies (MTA) were synthesized using the previously reported two-step soft-templating and ion-exchange chemical process.¹⁴ The meso-

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porous structure of MTA was investigated by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). Analysis of the TEM images gives an average particle size of ~ 7.8 nm for TiO₂ nanocrystals. In addition, N₂ adsorption–desorption measurements showed that the MTA catalyst contains narrow-sized mesopores between the nanoparticles. The specific Brunauer–Emmett–Teller (BET) surface area and the average pore diameter of MTA were calculated to be 157 m² g⁻¹ and 7.7 nm, respectively.¹⁴

Tetrabutylammonium decatungstate was synthesized and purified according to literature procedures.¹⁵ The [W₁₀O₃₂]⁴⁻ anions supported on mesoporous titania (DT-MTA) were prepared as follows: 1 g of Brij-58(HO(CH₂CH₂O)₂₀C₁₆H₃₃) surfactant was dissolved in 10 mL of anhydrous ethanol with stirring at room temperature. Then, 11 μ mol of tetrabutylammonium decatungstate ([Bu₄N]₄W₁₀O₃₂), 1.56 mmol of titanium tetrachloride (TiCl₄) and 5.55 mmol of titanium(IV) propoxide were slowly added to the surfactant solution with continuous stirring. The mixture was kept at room temperature for 2 h and then was transferred to a Petri dish and stored in an oven at 40 °C for 7 days. A mesoporous solid was prepared by heating the gel product at 100 °C under vacuum for 12 h, and then gently calcining in air to 260 °C for 4 h and, subsequently, to 350 °C for 6 h with a heating rate of 0.5 °C min⁻¹.

Physical characterization

Small-angle X-ray scattering (SAXS) measurements were performed on a Rigaku S-MAX 300 high-brilliance system using Cu K α radiation (80 kV and 40 mA). The sample-to-detector distance and center of the beam were precisely measured using a Ag-behenate standard ($d_{001} = 58.38$ Å). The two-dimensional diffraction images were integrated into a one-dimensional diffraction pattern, as a function of q , with the Fit2D program. The scattering data were corrected for dark current and empty tube scattering. Transmission electron microscopy (TEM) images were taken using a JEOL JEM-2100 electron microscope (LaB₆ filament) operating at an accelerated voltage of 200 kV (see Fig. S1, ESI†). Elemental compositions were obtained using a JEOL JSM-6390LV scanning electron microscope (SEM) operated at 20 kV. Data acquisition was performed using 100 s accumulation time. Nitrogen adsorption and desorption isotherms were measured at -196 °C with a Quantachrome Nova 3200e sorption analyzer. Before analysis, the samples were degassed at 150 °C under vacuum ($<10^{-4}$ mbar) for 12 h. The surface areas were calculated using the Brunauer–Emmett–Teller (BET) model on the adsorption data in the 0.05–0.25 relative pressure (P/P_0) range, the total pore volumes were calculated from the adsorbed amount at the $P/P_0 = 0.95$, and the distributions of pore size was derived from the adsorption branch of isotherms, using the non-local density functional theory (NLDFT) method for slit pore geometry (see Fig. S2, ESI†).

Photocatalytic reactions

The photosensitized oxidations of aryl alcohols 1–8 (0.1 mmol) (Fig. 1 and Table 1) were carried out in a solution of 3 mL of

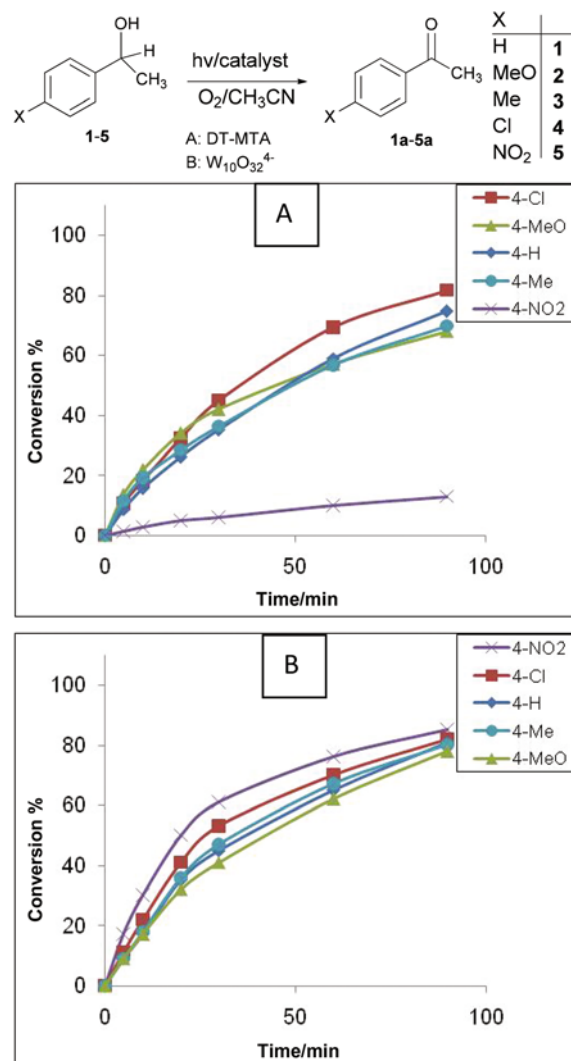
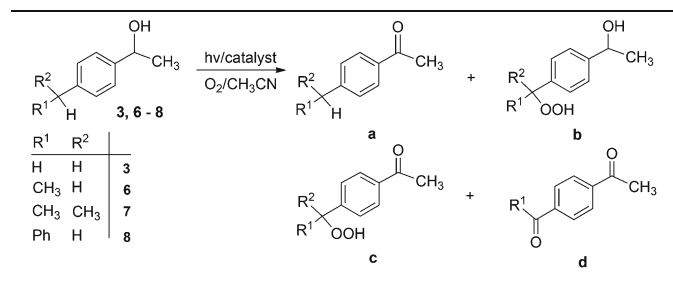


Fig. 1 Time profiles of *para*-substituted aryl alcohols (1–5) photooxidation over (A) mesoporous DT-MTA and (B) TBADT compound.

acetonitrile (HPLC-grade) in the presence of 45 mg of the catalyst in an open cap vial. Before switching on the lamp, the catalytic grains were kept in suspension by vigorous magnetic stirring for 10 min. Then the reaction mixture was irradiated for an appropriate time with a Variac Cermax 300 W xenon lamp ($\lambda > 320$ nm) as the light source under continuous bubbling with O₂ (*ca.* 20 mL min⁻¹). During irradiation, the reaction mixtures were cooled with ice water bath (*ca.* 5 °C). The reaction conversion and the assignment of products were determined by a combination of gas chromatography-mass spectrometry (Shimadzu GC-MS QP2010 Ultra) and ¹H and ¹³C NMR spectroscopy (Bruker AMX 300 MHz) by withdrawing small aliquots from the reaction mixture. To establish the identity of the products unequivocally, the retention times and spectral data from the crude aliquots were compared to those of commercially available compounds. Aryl alcohols 1–5 were commercially available, while alcohols 6–8 were synthesized following the literature procedure.¹⁶ The entire carbonyl

Table 1 DT-MTA and TBADT catalyzed photooxidation of the *para*-alkyl substituted 1-phenylethanols **3** and **6–8**

Sub.	Catalyst	Time (min)	Conversion ^a (%)	Relative product yield ^b (%)			
				a	b	c	d
3	TBADT	90	82	>99	—	—	—
3	DT-MTA	90	35	>99	—	—	—
6	TBADT	20	78	71	5	10	14
6	DT-MTA	90	41	90	7	—	3
7	TBADT	20	55	85	1	12	2
7	DT-MTA	90	51	91	2	4	3
8	TBADT	60	80	80	8	6	6
8	DT-MTA	90	35	92	—	—	2 ^c

^a Alcohol (0.1 mmol), decatungstate (5×10^{-4} M), 2 mL CH₃CN, at 5 °C.

^b Determined by ¹H NMR spectroscopy and GC-MS after reduction of hydroperoxides to the corresponding alcohols with PPh₃, error \pm 1%. ^c 6% of the corresponding 4-(1-hydroxyethyl) benzophenone was observed by NMR.

compounds were identical with the authentic samples based on NMR and GC-MS. Conversion of the alcohols and selectivity for the oxidation products were calculated as follows: conversion = $100 \times (C_o - C_t)/C_o$, selectivity = $100 \times (C_p/C_o - C_t)$ where, C_o , C_t are the initial and final (after time t) molar concentrations of alcohol, respectively and C_p is the concentration of the corresponding product at a certain time t of the photocatalytic reaction.

Results and discussion

Product analysis in the DT-MTA and TBADT catalyzed photooxidation of *para*-X substituted 1-phenylethanols 1–5

In order to test the catalytic activity of the DT-MTA we performed photooxidation of various *para*-X-substituted 1-phenylethanols 1–5 in the presence of molecular oxygen (Fig. 1A). It was found that 1-phenylethanols oxidized to the corresponding ketones (**1a–5a**) in appreciable yields (13–75%) within 1 h of irradiation, as identified by GC-MS and NMR spectroscopy, see Fig. 1. All the photocatalytic experiments were performed under similar conditions, using 0.1 mmol alcohol, 45 mg catalyst, 3 mL CH₃CN, 20 mL min⁻¹ O₂, at 5 °C, under UV-visible irradiation ($\lambda > 320$ nm). In consistent with the electrophilic character of the catalyst, the photooxidation of the *para*-methoxy and *para*-methyl 1-phenylethanols **2** and **3** gives ketones **2a** and **3a** with 70% and 75% conversion, respectively. On the other hand, electron-deficient alcohol **5** was oxidized to the corresponding ketone **5a** but in significantly lower yield (13%). To confirm that molecular oxygen is essential for

oxidation reactions, control experiments were conducted under similar conditions under a nitrogen atmosphere. The results showed no photocatalytic activity (2% conversion of **1** in 1 h was observed). Moreover, in the absence of the catalyst or visible light again no oxidation products were obtained, confirming that the oxidation reaction is really a photocatalytic process.

Besides the product evolution study, a formal kinetic analysis for the *para*-X-substituted 1-phenylethanols was also performed. Assuming that the oxygen concentration remains constant during the reaction process, the reaction can be considered as pseudo-first order with respect to the benzyl alcohol substrate (eqn (1)).

$$\ln(1 - x) = -kt \quad (1)$$

where k is the rate constant and x is the conversion of *para*-substituted benzyl alcohol at irradiation time t .

Thus, a plot of the $\ln(1 - x)$ versus time yields a straight line with the slope equal to the first-order reaction rate constant (k). As seen in Fig. S3 (ESI[†]), a remarkable affect is observed due to the nature of the *para*-substituent group, in which the photooxidation reaction proceeds faster as the electron-donating ability of the substituent group increases. For example, the photooxidation of **2** (MeO-substituted) proceeds faster than the corresponding oxidation of **1** (H-substituted), as inferred by the relative rate constant ratio of $k_{\text{MeO}}/k_{\text{H}} = 1.4$. In contrast the photooxidation of **5** (NO₂-substituted) proceeds with a lower rate constant than the oxidation of **1** with a ratio of $k_{\text{NO}_2}/k_{\text{H}} \sim 0.1$ (Fig. S3, ESI[†]). This result suggests that an electron transfer (ET) mechanism is predominant during the oxidation process.

In comparison, the [Bu₄N]₄W₁₀O₃₂ (TBADT) homogeneous photocatalyzed oxidations of the **1–5** alcohols were carried out on the same reaction scale as described above, using 1 mol% catalyst based on the amount of alcohol. In all cases, the corresponding *para*-substituted ketones (**1a–5a**) were produced in good-to-high isolated yields (78–85%) within 1 h of irradiation (Fig. 1B). Different from the above kinetic results using DT-MTA, homogeneous oxidation of aryl alcohols containing NO₂ and Cl (**5** and **4**) electron-withdrawing substitutes proceeds faster than the oxidation of *para*-methoxy 1-phenylethanol (**2**), *i.e.* bearing an electron-donor group (see Fig. S4, ESI[†]). This result suggests that a hydrogen atom transfer (HAT) mechanism is preferred for this system.⁸

Stability and reusability of the DT-MTA catalyst

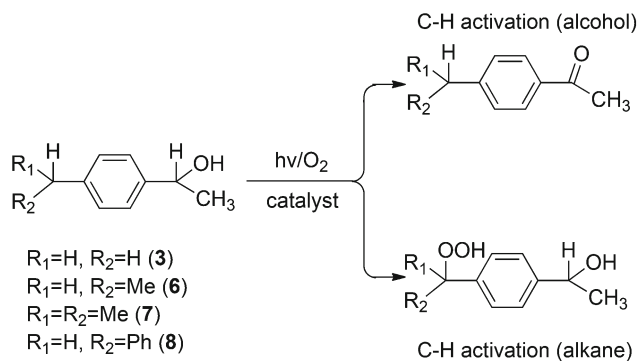
Because of the polymeric matrix of the DT-MTA, this catalyst can be easily recovered from the reaction mixture by simple filtration and it can be reused for the next catalytic run. The stability of the DT-MTA was examined by repeating the catalytic experiments, in which **3** was oxidized under the same reaction conditions described above. As shown in Fig. S5 (ESI[†]), the DT-MTA catalyst can be used at least three times without significant loss of its catalytic activity (\sim 85–78% conversion) and selectivity (100%). Elemental X-ray analysis (EDS) and N₂

physisorption results showed that the composition and the porous structure of the three times reused DT-MTA catalyst is well preserved after the oxidation reactions (results not shown), thereby, indicating high durability and recyclability.

Product analysis in the DT-MTA and TBADT catalyzed photooxidation of *para*-alkyl substituted 1-phenylethanols

So far, we have reported the catalytic behavior of the mesoporous DT-MTA and $[\text{Bu}_4\text{N}]_4\text{W}_{10}\text{O}_{32}$ (TBADT) compound with respect to the photooxidation of *para*-X-substituted 1-phenylethanols 1–5 that contain a benzylic hydrogen atom. To further study the applicability of these catalytic systems, a series of *p*-alkyl-substituted 1-phenylethanols, 6–8, were also oxidized under the same conditions. These substrates bear two distinguishable benzylic hydrogen atoms, one on the alcohol carbon and the other on the *para*-alkyl substituent, both of them can undergo C–H cleavage under the present conditions. According to this reaction scheme, a hydrogen atom abstraction or proton release in the case of a radical cation intermediate from the $\text{Ca}(\text{OH})\text{--H}$ group is expected to form the corresponding ketone, while similarly from the benzylic $\text{C}(\text{R})\text{--H}$ group of the *para*-substituent the deoxygenated product could be obtained, as shown in Scheme 1. Therefore, the selectivity of the catalyst by means of preferential hydrogen abstraction can be evaluated.

As shown in Table 1, both the catalytic systems showed a strong preference for oxidation of the carbon atom that bears the hydroxyl group, resulting in the formation of the corresponding aryl ketones 3a, 6a–8a. It is worth noting that the TBADT catalyzes the oxidation of the corresponding alcohols faster than the heterogeneous DT-MTA catalyst, although lower chemoselectivity was consistently observed, see Table 1. Indeed in these oxidation reactions, the selectivity depends on the nature of *para*-substituted group and the extent of the reaction time (see Table S1, ESI†). For instance, in the oxidation of 4-ethyl-1-phenylethanol (6) a highly selective formation of the corresponding ketone 6a was observed (71%) within a short irradiation time (20 min), while the corresponding 1,4-diketone (6d) was produced in 72% yield at a prolonged time (120 min) (see Table S1, ESI†). On the other hand,



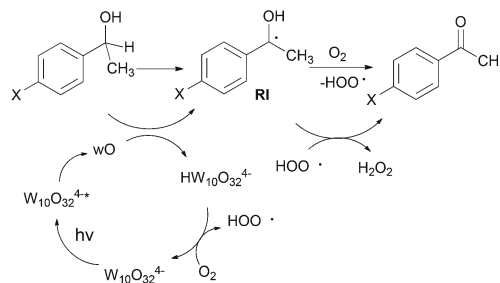
Scheme 1 Intramolecular selectivity in the C–H bond oxidation of *para*-alkyl substituted 1-phenylethanols.

the presence of a bulky isopropyl or phenyl group in alcohols 7 and 8 leads to a higher chemoselectivity, resulting in the formation of the corresponding ketones 7a and 8a in 85% and 80% yield, respectively. In the case of DT-MTA catalyzed photooxidations, although lower reaction rates were observed, a higher chemoselectivity to the corresponding ketones (3a and 6a–8a) was obtained (>90% relative yield, Table 1), thus allows the separation of the corresponding ketones in >99% isolated yields. These results reflect that there is a stronger and more consistent preference for C–H bond cleavage from the benzylic carbon compared with the *para*-alkyl substituent of 3 and 6–8 substrates. To rationalize these results, we propose that the polar surface of the solid support probably favors accumulation of the alcohol moiety, resulting in the selective oxidation to the corresponding ketones. It is worth noting that these results clearly demonstrate the important role of the present catalytic systems in synthetically useful oxidative transformations.

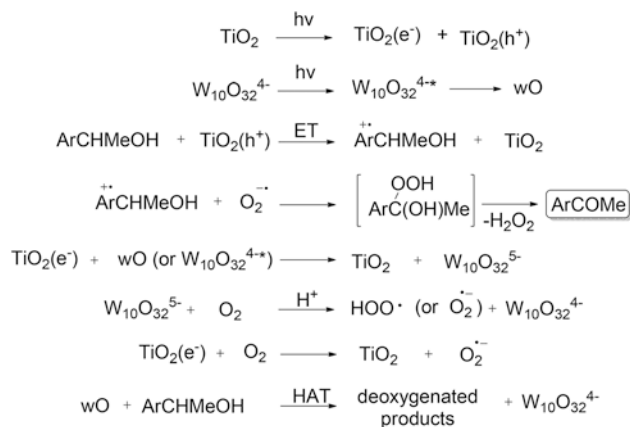
Proposed mechanistic pathways

Based on the product analysis and kinetic results, we suggest that the decatungstate-catalyzed homogeneous oxidation of benzyl alcohols proceeded *via* a HAT mechanism. Accordingly, a HAT can be realized from the substrate to the excited state of the catalyst (wO), leading to the formation of an alpha-hydroxy carbon-centered radical intermediate (RI) and the reduced form of the catalyst $\text{HW}_{10}\text{O}_{32}^{4-}$. The latter can be re-oxidized by molecular oxygen, producing hydroperoxy radicals ($\text{HOO}\cdot$), whereas the RI intermediate can be trapped by O_2 or the *in situ* produced $\text{HOO}\cdot$ to form the corresponding aryl ketone (Scheme 2). This proposed oxidation pathway is consistent with previous mechanistic studies on the oxidation of aromatic alcohols with $\text{W}_{10}\text{O}_{32}^{4-}$.¹⁷

Regarding the DT-MTA catalyzed aerobic oxidation of aryl alcohols, a reasonable mechanistic pathway can be assessed by the kinetics and selectivity of the reactions. On the basis of these results, we conclude that aromatic alcohols are oxidized on DT-MTA by the reaction routes shown in Scheme 3. First, the TiO_2 nanocrystals are excited under the UV-vis irradiation to generate the $\text{TiO}_2(\text{e}^-)$ and $\text{TiO}_2(\text{h}^+)$ pairs. Subsequent oxidation of $\text{TiO}_2(\text{e}^-)$ by electron transfer to molecular oxygen can produce the superoxide anions ($\text{O}_2^{\cdot-}$). Although an electron transfer can also be realized from the



Scheme 2 Proposed mechanisms for the photooxidation of *para*-substituted aryl alcohols catalyzed by the decatungstate anion.



Scheme 3 Proposed mechanistic pathway for the photocatalyzed oxidation of aryl alcohols over mesoporous DT-MTA.

conduction band of TiO_2 (-0.5 V vs. NHE) to the lowest unoccupied molecular orbital (LUMO) of decatungstate clusters (or to the long-lived intermediate wO),¹⁸ leading to the formation of $\text{W}_{10}\text{O}_{32}^{5-}$ reduced species. Once these species are produced, they can be readily re-oxidized by molecular oxygen, forming hydroperoxy and/or superoxide anion radicals. On the other hand, the $\text{TiO}_2(h^+)$ holes can induce the oxidation of alcohols producing the corresponding cationic radicals (ArOH^+). Finally, these radical intermediates can be further reacted with *in situ* produced superoxide anions to form the corresponding carbonyl products. However, under our irradiation conditions ($\lambda > 320$ nm), $\text{W}_{10}\text{O}_{32}^{4-}$ are also be excited to the locally excited state $\text{W}_{10}\text{O}_{32}^{4-*}$, which undergoes fast decay to the relatively long lived intermediate wO .^{8,18} Subsequent hydrogen atom abstraction from the benzylic position of the alcohol produces the one-electron-reduced species $\text{H}^+\text{W}_{10}\text{O}_{32}^{5-}$ and a radical intermediate. Thus, a HAT route between the excited states of wO and aryl alcohols cannot be excluded, giving a significant amount of the observed deoxygenated products.

Conclusions

In conclusion, the aerobic photooxidation of various aryl alcohols by the $[\text{Bu}_4\text{N}]_4\text{W}_{10}\text{O}_{32}$ (TBADT) complex and $\text{W}_{10}\text{O}_{32}^{4-}$ supported on mesoporous TiO_2 nanoparticle assemblies (DT-MTA) has been reported. Our experiments showed that both catalytic systems are highly active and selective for the oxidation of aryl alcohols, under mild conditions. The DT-MTA used in oxidation reactions was found to be stable and active under the present conditions, providing a unique system that combines long-term stability and high activity. From the mechanistic point of view, a HAT mechanism was proposed for the decatungstate catalyzed oxidations, while an ET mechanism was predominated for the oxidation reactions over the DT-MTA catalyst. Synthesis and catalytic applications of different POM-supported mesoporous TiO_2 nanoparticle assemblies are in progress.

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