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Immobilization of $(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ on Mesoporous MCM-41 and Amorphous Silicas for Photocatalytic Oxidation of Cycloalkanes with Molecular Oxygen

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Heterogenization of $(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ on amorphous and MCM-41 silicas by impregnation is a suitable method to prepare efficient and stable catalysts able to oxidize unactivated C–H bonds to the corresponding alcohols and ketones with molecular oxygen and near ultraviolet light. The thus-prepared catalysts were characterized by spectroscopic and N_2 adsorption–desorption experiments. A better dispersion of decatungstate was achieved with MCM-41, which also has the higher surface area. Results obtained in the model photooxidation of cyclohexane and cyclododecane confirm that the decatungstate heterogenized on the more ordered MCM-41 silica promotes the process with higher chemoselectivity (cyclohexanone/cyclohexanol molar ratio = 2.6). The photocatalytic efficiency of $(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ is not reduced after heterogenization; moreover, decatungstate immobilized on amorphous silica oxidizes cyclododecane with a markedly higher efficiency than in the homogeneous phase. The supported photocatalysts can be used at least three times without any loss of activity. © 2002 Elsevier Science (USA)

Key Words: **photocatalysis; polyoxotungstates; mesoporous materials; oxidative catalysis; hydrocarbon oxidation.**

1. INTRODUCTION

Catalytic oxidation represents a fundamental route to the industrial preparation of functionalized hydrocarbons and fine chemicals (1–3). Unfortunately many catalytic oxidations are accompanied by drawbacks such as low yield, limited catalyst stability, and the production of large amounts of pollutant materials (4). Because of increasingly stringent environmental regulations, the use of robust heterogeneous and/or supported catalysts that can promote selective oxidation by inexpensive reagents without generating toxic waste has been extensively studied by academic as well as industrial research groups and represents today an ever-expanding area of interest (5). Many examples are based on the use of inorganic molecular sieves. Alkanes can be oxidized with H_2O_2 over TS-1 between 323 and 373 K to alcohols and ketones (6). Cobalt- and chromium-substituted molecular sieves (CoAPO and CrAPO) are used as catalysts in the oxidation of cyclohexane and *n*-hexane with molecular oxygen in acidic media (7, 8).

A further class of heterogeneous catalysts utilized in hydrocarbon oxidation is composed of catalytically active metal complexes immobilized within a zeolite matrix according to the ship-in-the-bottle strategy (9). The durable anchoring of the complex to the molecular sieve is mainly achieved by electrostatic retention, spatial entrapment, and low solubility. Even if different transition-metal complexes have been entrapped in molecular sieves, the main interest of researchers has focused on metal complexes with oxidation-resistant aromatic ligands such as phthalocyanines (10), polypyridines (11), salen derivatives (12, 13), and metalloporphyrins (14, 15). The ship-in-the-bottle complexes (so-called inorganic enzymes) (16) played an important role in the rational design of catalysts. Unfortunately, in many cases it is difficult to entrap the metal complex in the supercages of the zeolite due to the tendency of the metal to lose its ligands and to be leached into solution (17).

Among the oxidation catalysts, polyoxometalates have attracted much attention in the last two decades. The main reason is due to their variety and high potential as catalysts useful in solution as well as in heterogeneous conditions (18). We and other authors previously demonstrated that polyoxometalates have a noticeable activity in the photoinduced oxidation of numerous organic compounds, including hydrocarbons (19–28). In particular, the reaction mechanism that is generally accepted for the oxidation of an alkane by the photoexcited $W_{10}O_{32}^{4-}$ is schematized in the case of cyclohexane by Eqs. [1]–[7] in Scheme 1.

The photoexcited decatungstate is able to initiate the oxidation of the substrate through hydrogen abstraction

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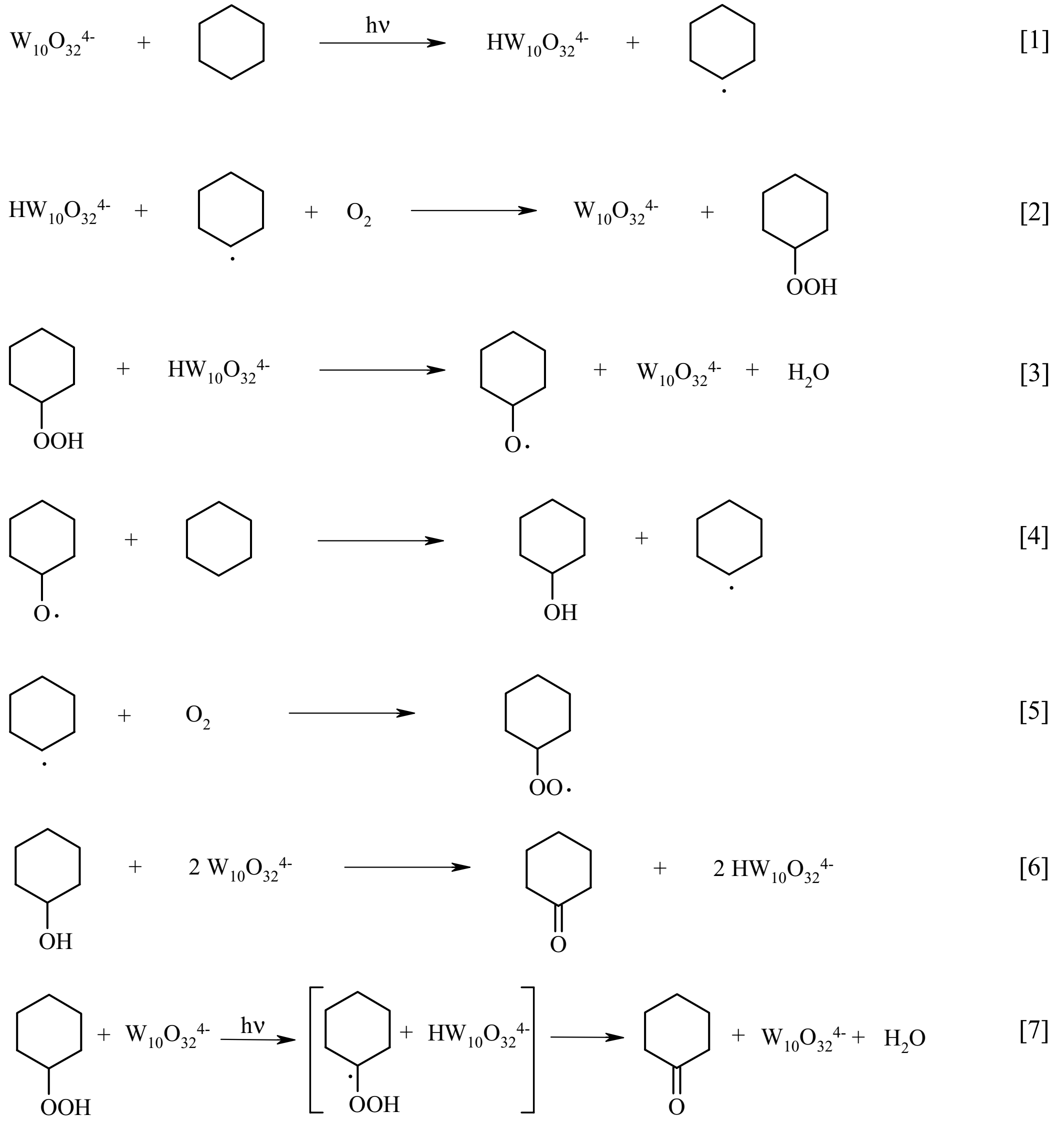


SCHEME 1. Reaction mechanism for the oxidation of cyclohexane by photoexcited (n-Bu$_4$N)$_4$W$_{10}$O$_{32}$.

(Eq. [1]). The formation of intermediates and final products occurs mainly according to a photocatalytic cycle (Eqs. [2]–[7]) that involves the decatungstate both in the oxidized and in the photoreduced forms. $W_{10}O_{32}^{4-}$ is regenerated by O_2, which, in turn, undergoes a reductive activation process.

Recent developments in the use of inorganic polymeric materials and in particular of mesoporous MCM-41-type materials as inorganic supports for both organic (29–31) and inorganic (32–35) catalysts prompted us to investigate the preparation and the activity of heterogeneous photocatalysts based on the immobilization of (n-Bu$_4$N)$_4$W$_{10}$O$_{32}$ on this material, which consists of uniform and hexagonal arrays of mesopores ranging from 20 to 100 Å (36, 37) and shows a high surface area (~1000 m^2/g). These features permit the introduction of large molecules on MCM-41 with minimum hampering of diffusion of reagents and products through pores and channels. Consequently, among the large number of solid supports for catalytically active metal oxide clusters recently introduced, the mesoporous MCM-41 is one of the most utilized and studied (38–41). Previous investigations have demonstrated that polyoxometallates can be supported on MCM-41 (42–48).

In this work (n-Bu$_4$N)$_4$W$_{10}$O$_{32}$ is successfully immobilized on both MCM-41 and amorphous silica by a simple impregnation process. A physicochemical investigation of the so obtained heterogeneous catalysts is carried out by spectroscopic and N$_2$ adsorption–desorption techniques and the photocatalytic properties are assessed in the oxidation of two simple representative alkanes, cyclohexane and cyclododecane. The selective oxidation of these hydrocarbons is an important goal in applied synthesis since the production of cyclohexanone from cyclohexane continues to be an important challenge of industrial interest (49, 50) and cyclododecanone is a precursor in the synthesis of naturally occurring fragrances (51).

2. EXPERIMENTAL

2.1. Materials

Reagents, solvents, and standards were purchased in the highest purities available and used without further purification: dichloromethane, acetonitrile, cyclohexane, cyclohexanol, cyclohexanone, cyclododecanol, cetyltrimethylammonium chloride (25% wt sol. in water), and sodium silicate (27% SiO_2, 14% NaOH in water) from Aldrich; cyclododecane and cyclododecanone from Lancaster; tetramethylammonium hydroxide (25% wt sol. in water), sodium tungstate dihydrate, and tetrabutylammonium bromide from Fluka; and SiO_2 (fumed colloidal silica, 0.012 μm) from Strem Chemicals (SiO_2SC).

2.2. Catalysts Preparation

MCM-41 silica was prepared following a modification of a reported procedure (6). In a 500-ml round-bottom flask at room temperature sodium silicate solution (27% SiO_2, 14% NaOH in water) (32 ml), tetramethylammonium hydroxide solution (25% in water) (17 ml), cetyltrimethylammonium chloride solution (25% in water) (68 ml), concentrated sulfuric acid (4 ml), and water (120 ml) were vigorously stirred for 3 h. The final compositions of the gel was $SiO_2 \cdot 0.39Na_2O \cdot 0.25CTMACl \cdot 0.24TMAOH \cdot 50.7H_2O$. The gel was hydrothermally aged at 100°C for 4 days in a teflon bottle, and the resulting solid was filtered on a Buchner filter, washed with distilled water (1 L), air dried, and calcined at 540°C for 8 h.

According to a literature procedure (52), $(n\text{-}Bu_4N)_4W_{10}O_{32}$ was prepared by mixing hot solutions of $Na_2WO_4 \cdot 2H_2O$ (4 g) in water (25 ml) and 3 M HCl (8 ml). To the clear yellow solution obtained after boiling for 5 min, an aqueous solution of tetrabutylammonium bromide (1.6 g/ 3 ml) was added, giving a white precipitate which was filtered, washed with boiling water (15 ml) and ethanol (15 ml) and then with diethyl ether (15 ml), and recrystallized from hot DMF.

$(n\text{-}Bu_4N)_4W_{10}O_{32}$ was heterogenized on silica following a known "impregnation" procedure (53). The catalyst (0.1 g) is dissolved in CH_3CN (6 ml) and the siliceous support (SiO_2SC or MCM-41 silica) (1 g) was added. The suspension was stirred at 333 K for 2 h. The CH_3CN was eliminated warming up to 353 K and the obtained powder was then dried under high vacuum for 2 h, affording the final heterogeneous catalyst, which contains about 10% (w/w) decatungstate (SiO_2SC/W10%, MCM-41/W10%). Following the same procedure, catalysts with higher loading were prepared using 0.3 and 0.6 g of $(n\text{-}Bu_4N)_4W_{10}O_{32}$ (SiO_2SC/W30%, MCM-41/W30% and SiO_2SC/W60%, MCM-41/W60%, respectively).

2.3. Catalyst Characterization

IR spectra of all the catalysts (KBr pellets) were recorded with a Nicolet 510 FT-IR instrument, fitted with a Spectra-Tech collector diffuse reflectance accessory (range from 4000 to 200 cm^{-1}). Spectrophotometric measurements were performed with a Perkin–Elmer Lambda 6, UV–vis spectrometer equipped with an integrating sphere.

N_2 adsorption–desorption experiments were carried out at 77 K on a Micromeritics ASAP 2010. Before each measurement the sample was outgassed at 423 K and 1.33×10^{-3} Pa for 12 h. The N_2 isotherms were used to determine the specific surface areas, SA_{BET}. The pore volume distribution was calculated by the classic Kelvin equation using the cylindrical pore geometry and the Broekhoff–de Boer model.

2.4. Photocatalytic Reactions

Photochemical excitations were performed with a Helios Italquartz Q400 medium-pressure mercury lamp (light intensity 15 mW cm^{-2}), selecting wavelengths higher than 300 nm with a cutoff filter, at room temperature (298 ± 1 K) and 101.3 k Pa of O_2. Heterogenized $(n\text{-}Bu_4N)_4W_{10}O_{32}$ (15 g/L) was kept in suspension under magnetic stirring at 1000 rpm in 3 ml of CH_2Cl_2 containing cyclohexane or cyclododecane (10 mmol) and irradiated for 120 min inside a Pyrex reactor. After irradiation, the sample was centrifuged, the products that remained adsorbed on the irradiated powders were extracted with CH_2Cl_2 (3×3 ml), and the organic phases were analyzed by a gas chromatographic technique using a HP 6890 Series instrument equipped with a flame ionization detector and a HP-WAX (cross-linked polyethylene glycol, 30 m; 0.32 mm × 0.5 μm film thickness) capillary column [isotherm at 373 K for cyclohexane and 433 K (1 min), 2 K/min, 443 K (8 min) for cyclododecane]. Quantitative analysis has been carried out with calibration curves obtained with authentic samples. Each photocatalytic experiment was repeated four times in order to evaluate the errors.

Irradiations in homogeneous solution were carried out dissolving $(n\text{-}Bu_4N)_4W_{10}O_{32}$ (0.2 mmol) in CH_2Cl_2/CH_3CN 2/1 (3 ml) and adding cyclohexane or cyclododecane (10 mmol) under the experimental conditions described for the heterogeneous systems.

The employed amount of decatungstate warranted that all the incident photons were absorbed.

No oxidation products were observed when blank experiments both in homogeneous phase and with the heterogeneous systems were run in the absence of light or irradiating the unmodified supports.

3. RESULTS AND DISCUSSION

3.1. *Structural Characterization of Heterogenized* $(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$

Spectroscopic evidences showed that $(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ is located on the surface of MCM-41 as well as amorphous silica. The UV–vis results revealed that the $\text{W}_{10}\text{O}_{32}^{4-}$ unit is present on the surface of the supports without any modification (absorption at 325 nm). The infrared spectrum of MCM-41/W10% reported in Fig. 1 shows the characteristic bands of $\text{W}_{10}\text{O}_{32}^{4-}$ ($\nu = 802, 1486\ \text{cm}^{-1}$) as well as those typical of the employed alkylammonium cation (C–H bond stretching at about 2870 cm^{-1}). Analogous results were obtained with amorphous silica.

We have already reported that adsorption of $(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ on silica occurs through electrostatic interactions (28). In fact, the solvent used in the impregnation procedure should favor the formation of ion pairs between the decatungstate anion and the quaternary ammonium cation (54), and these cations may act as a bridge between the surface and the decatungstate (55). This interpretation is supported by previous investigations on the modes of polyoxomolybdate adsorption on silica in a nonacid environment (56).

3.2. *Textural Characterization of Catalysts*

The MCM-41 is an ordered mesoporous molecular sieve, well described in literature (36, 37), with a structure that consists of an assemblage of nonintersecting tubular pores. The pore structure is composed of a hexagonal array of uniform channels of controlled size. Since 1992 (57) N_2 physisorption isotherms have been used to characterize the porosity of this type of material. The adsorption–desorption isotherm of the MCM-41 used as support to immobilize $(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ is typical, as described by Mobil researches (36, 37). The sample has a BET surface area of about 1200 m^2/g and the pore diameter is approximately 3 nm. The N_2 adsorption–desorption of MCM-41 exhibits a reversible type IV isotherm with a narrow hysteresis loop at $p/p^\circ > 0.5$ and a sharp pore filling step at ca. $p/p^\circ = 0.35$, characteristic of uniform pores. After the impregnation with $(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$, all samples still show a reversible type IV isotherm and a sharp inflection at $p/p^\circ \sim 0.35$ but no hysteresis loop. In Table 1 the BET surface areas, the total pore volumes, and the pore distribution of the MCM-41 before and after the immobilization of $(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ on this material are summarized.

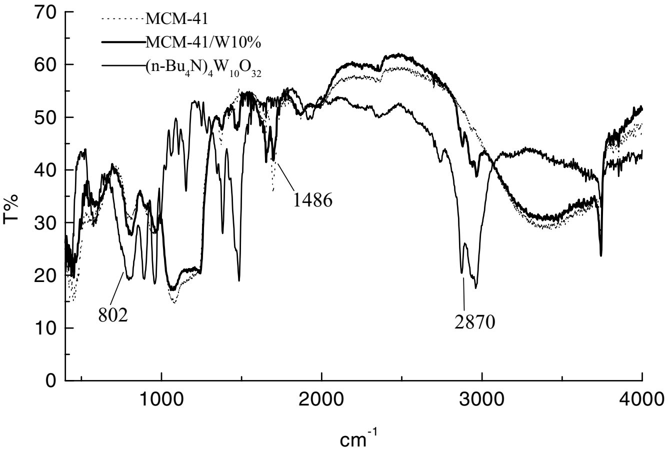


FIG. 1. IR spectra of MCM-41, of $(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$, and of the heterogeneous system MCM-41/W10%.

TABLE 1

Specific Surface Area, Total Pore Volume, and Pore Volume Distribution of MCM-41 before and after Impregnation with Decatungstate

	$\text{SA}_{\text{B.E.T.}}$ (m^2/g)	V_{tot}[a] (cm^3/g)	Pore distribution (cm^3/g) 0–2 nm	2–4 nm	4–10 nm	>10 nm
MCM-41	1240.5	1.130	0.007	0.775	0.154	0.194
MCM-41/W10%	1110.8	0.951	0.000	0.802	0.051	0.098
MCM-41/W30%	824.9	0.680	0.000	0.585	0.036	0.059
MCM-41/W60%	624.1	0.471	0.000	0.400	0.046	0.025

[a] Amount adsorbed at $p/p^\circ = 0.95$.

A general decrease in surface area and in total pore volume with increasing amounts of $(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ was found. After the adsorption of $(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ [10% (w/w), sample MCM-41/W10%], the fraction of the pore volume attributable to cavities more than 4 nm in diameter decreases, giving an apparently more ordered material (85% of the porosity ranges between 2 and 4 nm). This clearly indicates that $(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ fills first the largest pores, although its size should allow it to enter the 2- to 4-nm channels (58, 59). Only when more decatungstate was added were the uniform channels of the support with pore sizes of 3 nm also filled. The MCM-41/W30% and MCM-41/W60% samples show a decrease both in surface area and in pore volume but the pore percentage in the 2- to 4-nm range remains constant (about 85%), proving that the decatungstate enters the ordered mesopore.

Table 2 shows the BET surface area, the total pore volume, and the pore distribution of amorphous silica SiO_2SC impregnated with decatungstate. All the samples show, as expected, a disordered pore distribution.

In this case the size of the majority of the pores is estimated to be larger of 10 nm. When the support is impregnated with $(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ both the surface area and the pore volume strongly decrease, with the last decreasing uniformly in the whole porosity range. When the SiO_2SC support is used, the hybrid materials loaded with 10 and 30% decatungstate (SiO_2SC/W10% and SiO_2SC/W30%) resulted in similar surface areas and pore volumes. This suggests that, in the SiO_2SC/W30% sample, further added decatungstate is not uniformly dispersed on the

TABLE 2

Specific Surface Area, Total Pore Volume, and Pore Volume Distribution of SiO_2SC before and after Impregnation with Decatungstate

	$SA_{B.E.T.}$ (m^2/g)	V_{tot}[a] (cm^3/g)	Pore distribution (cm^3/g)			
			0–2 nm	2–4 nm	4–10 nm	>10 nm
SiO_2SC	95.2	0.225	0.000	0.000	0.021	0.204
SiO_2SC/W10%	53.6	0.131	0.000	0.001	0.009	0.121
SiO_2SC/W30%	53.7	0.160	0.000	0.005	0.008	0.147
SiO_2SC/W60%	40.0	0.105	0.000	0.005	0.008	0.092

[a] Amount adsorbed at $p/p^\circ = 0.95$.

support but, likely, undergoes aggregation phenomena. The SiO_2SC/W60% sample which contains 60% of (n-$Bu_4N)_4W_{10}O_{32}$ loses more than 50% of the initial porosity.

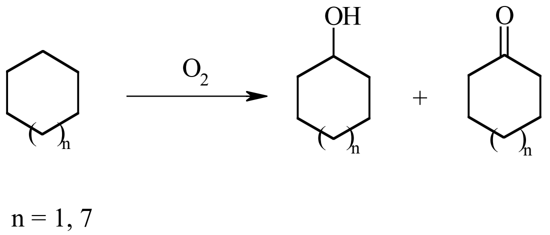
3.3. Photocatalytic Activity

The photocatalytic activity of (n-$Bu_4N)_4W_{10}O_{32}$ supported on MCM-41 and amorphous silica has been assessed studying the O_2-oxidation of cyclohexane and cyclododecane. Irradiation of (n-$Bu_4N)_4W_{10}O_{32}$ both in the heterogeneous systems and in homogeneous phase induces the oxidation of the two alkanes to the corresponding alcohols and ketones as main stable products (more than 90% of the overall oxidized substrate) according to Eqs. [1]–[7] (Scheme 1) and Scheme 2.

Iodometric analysis gave evidence that hydroperoxides, which are the primary products during the oxygenation of alkanes by illuminated (n-$Bu_4N)_4W_{10}O_{32}$ (Eq. [2]) (24), were accumulated only in negligible amounts (less than 5%). The possibility of oxidizing cyclododecane with photoexcited (n-$Bu_4N)_4W_{10}O_{32}$ is demonstrated in this work for the first time.

The results of GC analyses after 120 min of irradiation are reported in Table 3 in terms of overall yield and ketone-to-alcohol molar ratio.

A comparison between entries 1 and 2 (Table 3) indicates that the most significant difference between the photooxidation processes of cyclohexane and cyclododecane under homogeneous conditions concerns chemoselectivity, with the formation of a higher amount of ketone in the case of cyclododecane. In these experiments we were forced to employ a CH_2Cl_2/CH_3CN mixture in order to dissolve both (n-$Bu_4N)_4W_{10}O_{32}$ and cycloalkane in the same solution. A main advantage of using the decatungstate in its heterogenized forms is represented by a wider choice of dispersing medium.



SCHEME 2. Substrates employed and their oxidation products.

Irradiation of CH_2Cl_2 dispersions of heterogenized (n-$Bu_4N)_4W_{10}O_{32}$ induces the oxidation of cyclohexane and cyclododecane, leading to the formation of the same products obtained in homogeneous conditions but in different ratios. As far as the stability of the heterogeneous photocatalysts is concerned, they can be employed at least three times without suffering any appreciable loss of photocatalytic activity.

Different factors affecting efficiency and selectivity of the photooxidation processes,such as heterogenization, morphology of the support, and decatungstate loading, were investigated.

3.3.1. Effect of the amount of the heterogeneous photocatalysts. Photochemical experiments were carried out varying the amount of suspended photocatalysts. The yield in oxidation products after 2 h of irradiation sharply raised the amount of dispersed powder to a limit which corresponds to the maximum amount of photocatalyst that allowed all the particles to be totally illuminated. For higher amounts of heterogenized decatungstate the concentration of oxidized alkane decreased, likely because of a screening effect by excess particles which masks part of the photosensitive surface. An optimum amount of 15 mg/ml for all the employed photocatalysts was chosen in order to ensure maximum absorption of light and maximum efficiency.

TABLE 3

Photocatalytic Oxidation of Cyclohexane and Cyclododecane

Entry	Photocatalytic system[a]	Substrate (1×10^{-2} mol L^{-1})	Yield[b] (%)	Ketone/alcohol (molar ratio)
1	(n-$Bu_4N)_4W_{10}O_{32}$[c]	Cyclohexane	23 ± 3	0.5 ± 0.05
2	(n-$Bu_4N)_4W_{10}O_{32}$[c]	Cyclododecane	19 ± 2	1.0 ± 0.07
3	SiO_2SC/W10%[d]	Cyclohexane	20 ± 2	2.1 ± 0.17
4	MCM-41/W10%[d]	Cyclohexane	18 ± 1	2.6 ± 0.20
5	SiO_2SC/W30%[d]	Cyclohexane	18 ± 1	1.1 ± 0.02
6	MCM-41/W30%[d]	Cyclohexane	21 ± 2	2.4 ± 0.10
7	SiO_2SC/W60%[d]	Cyclohexane	9 ± 1	1.0 ± 0.05
8	MCM-41/W60%[d]	Cyclohexane	14 ± 1	1.0 ± 0.05
9	SiO_2SC/W10%[d]	Cyclododecane	46 ± 1	2.1 ± 0.10
10	MCM-41/W10%[d]	Cyclododecane	15 ± 1	2.3 ± 0.15
11	SiO_2SC/W30%[d]	Cyclododecane	20 ± 2	1.1 ± 0.15
12	MCM-41/W30%[d]	Cyclododecane	15 ± 1	2.4 ± 0.15

[a] 120-min irradiation at excitation wavelengths higher than 300 nm. Light intensity, 15 mW cm^{-2}; volume of irradiated solutions or powder dispersions, 3 ml; temperature, 298 ± 1 K; pressure, 101.3 kPa of O_2.

[b] Overall percentage yields to both alcohol and ketone after 120-min irradiation.

[c] 2×10^{-4} mol L^{-1} of $W_{10}O_{32}^{4-}$ dissolved in CH_2Cl_2/CH_3CN (2 : 1 v/v).

[d] 15 g L^{-1} for heterogeneous photocatalysts dispersed in CH_2Cl_2.

3.3.2. Oxidation yields. Entries 3 and 4 of Table 3 report the yields for the photoinduced oxygenation of cyclohexane with SiO_2SC/W10% and MCM-41/W10% catalysts, respectively. A comparison with the results obtained in homogeneous solution (entry 1) allows us to infer that heterogenization with both amorphous and MCM-41 silicas does not significantly affect the photochemical efficiency of (n-$Bu_4N)_4W_{10}O_{32}$. This represents an interesting result in view of the employment of these systems in heterogeneous catalysis, where, normally, the easy removal of the catalysts from the dispersing medium compensates for their loss of activity in comparison with the homogeneous phase.

The above results imply that, in agreement with those discussed in Section 3.2, both solid supports are able to disperse 10% decatungstate, thus avoiding aggregation phenomena that should reduce the efficiency of the photocatalyst. The negative effect of the formation of aggregates on the photocatalytic activity of the decatungstate is confirmed by control experiments in which (n-$Bu_4N)_4W_{10}O_{32}$ was suspended as a solid in CH_2Cl_2. Under these conditions, irradiation led to the oxidation of the investigated alkanes with yields about 10 times lower than those reported in Table 3.

Mesoporous MCM-41/W10% is characterized by a surface area much higher than that of SiO_2SC/W10%. Consequently, it should be able to better disperse higher amounts of added decatungstate, thus supporting a greater number of photocatalytic sites without forming aggregates. Indeed an increase in the decatungstate loading from 10 to 30% resulted in a higher photochemical efficiency only in the case of MCM-41 (entries 5, 6). On the other hand, a significant decrease in activity due to aggregation phenomena is observed on both supports by increasing the decatungstate loading up to 60% (entries 7, 8).

It is interesting that the SiO_2SC/W10% photocatalyst is able to induce the oxidation of cyclododecane with double efficiency compared with that obtained in the homogeneous phase (entry 9). The different reactivity of cyclohexane and cyclododecane in the presence of photoexcited SiO_2SC/W10% is most likely due to surface effects, which can control in different ways the local concentration of the hydrocarbons at the surface, where the photoactive decatungstate is immobilized. In fact, although the interactions of alkanes with the hydroxylated surface of silica have been shown to be very weak and nonspecific (60), cyclododecane is expected to be more adsorbed than cyclohexane because of its higher size. This statement has been confirmed by GC analyses of not-irradiated dispersions of SiO_2SC/W10% in CH_2Cl_2 containing cyclohexane or cyclododecane. After 120 min the concentration of cyclododecane in the solution decreased from 10 to 8.9×10^{-3} mol L^{-1}, while when the same experiment was carried out with cyclohexane the concentration in solution decreased from 10 to 9.3×10^{-3} mol L^{-1}. The positive effect of the matrix on the reactivity of cyclododecane was not observed with MCM-41/W10% (entry 10), probably because the free surface is mostly localized within pores of 3 nm, where the decatungstate is not adsorbed.

3.3.3. Chemoselectivity of the oxidation processes. Heterogenization with both amorphous and MCM-41 silicas is a suitable means of controlling the chemoselectivity of alkane photooxidation processes by (n-$Bu_4N)_4W_{10}O_{32}$. In particular, we observed that the ketone/alcohol ratio increases significantly when decatungstate is loaded on the solid supports, reaching a maximum value of 2.6 for the cyclohexane oxidation with MCM-41/W10%. Generally speaking, the influence of solid matrices on the selectivity of catalytic processes may in part be ascribed to their ability to control surface reactions modifying adsorption–desorption equilibria of reagents, reaction intermediates, and products (61, 62). More specifically, the polar surface of the siliceous supports is expected to favor the accumulation of produced alcohols at the interfaces and, consequently, their well-known (63) oxidation to ketones by the photoexcited decatungstate (Eq. [6]). Indeed, cyclohexanol and cyclododecanol (1×10^{-2} mol L^{-1}) dissolved in heptane were found to undergo oxidation to the corresponding ketones in the presence of photoexcited SiO_2SC/W10% or MCM-41/W10%.

4. CONCLUSIONS

Evidence of heterogenization of (n-$Bu_4N)_4W_{10}O_{32}$ on amorphous and MCM-41 silicas have been provided by spectroscopic and N_2 adsorption–desorption experiments. As MCM-41 has a surface area much higher than that of amorphous silica, it allows a better dispersion of decatungstate and its ordered structure is maintained after impregnation of the decatungstate up to 60%. Progressive impregnation of the decatungstate molecules up to 30% (w/w) on such material resulted in a large amount of scattered, accessible, well-spaced, and structurally well-defined active sites. Heterogenization of (n-$Bu_4N)_4W_{10}O_{32}$ on both amorphous and MCM-41 silicas is a suitable means of preparing efficient and stable catalysts able to oxidize unactivated C–H bonds to the corresponding alcohols and ketones with molecular oxygen and near-ultraviolet light. The morphology of the support plays a key role in affecting the photocatalytic activity of the decatungstate from both the overall oxidation yield and the chemoselectivity points of view. The photocatalytic efficiency of (n-$Bu_4N)_4W_{10}O_{32}$ is not reduced after heterogenization; moreover, SiO_2SC/W10% is able to oxidize cyclododecane with a markedly higher efficiency than in the homogeneous phase. The supported photocatalysts can be used at least three times without any loss of activity. As far as the chemoselectivity of the photooxidation processes is concerned, the nature of the solid matrix may control the ketone/alcohol ratio of the photooxidation processes through modification of adsorption–desorption equilibria of reagents and reaction intermediates. In particular, the mesoporous material favors the reaction of the alcoholic intermediates with the photoactive decatungstate to the corresponding ketones.

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REFERENCES

1. Albonetti, S., Cavani, F., and Trifirò, F., *Catal. Rev.–Sci. Eng.* **38**, 413 (1996).
2. Arends, I. W. C. E., Sheldon, R. A., Wallau, M., and Schuchardt, U., *Angew. Chem. Int. Ed. Engl.* 144 (1997).
3. Sheldon, R. A., *CHEMTECH* 566 (1991).
4. Sheldon, R. A., and Kochi, J. K., "Metal-Catalyzed Oxidations of Organic Compounds." Academic Press, New York, 1981.
5. De Vos, D. E., Buskens, P. L., Vanoppen, D. L., Knops-Gerrits, P. P., and Jacobs, P. A., *in* "Comprehensive Supramolecular Chemistry," Vol. 7, p. 647, Pergamon, Elmsford, NY, 1996.
6. Huybrechts, D. R. C., De Bruycher, L., and Jacobs, P. A., *Nature* **345**, 240 (1990).
7. Liu, S., and Weng, H., *Appl. Catal. A* **118**, 21 (1994).
8. Kraushaar-Czarnetski, B., Hoogevorst, W. G. M., and Stork, W. H. J., *Stud. Surf. Sci. Catal.* **84**, 1869 (1994).
9. Herron, N., and Corbin, D. R., Guest Eds., *J. Incl. Phenom.* **21** (1995).
10. Parton, R. F., Vankelecom, I. F. J., Casselman, M. J. A., Bezonkhanova, C. P., Uytterhoeven, J. B., and Jacobs, P. A., *Nature* **370**, 541 (1994).
11. Knops-Gerrits, P. P., De Vos, D. E., Thibault-Starzyk, F., and Jacobs, P. A., *Nature* **369**, 543 (1994).
12. Ogunwumi, S. B., and Bein, T., *J. Chem. Soc. Chem. Commun.* 901 (1997).
13. Sabater, M. J., Corma, A., Domenech, A., Fornes, V., and Garcia, H., *J. Chem. Soc. Chem. Commun.* 1285 (1997).
14. Zhan, B. Z., and Li, X. Y., *Chem. Commun.* 349 (1998).
15. Battioni, P., Iwanejko, R., Mansuy, D., Mlodnicka, T., Poltowicz, J., and Sanchez, F., *J. Mol. Catal. A* **109**, 91 (1996).
16. Mitchell, P. C. H., *Chem. Ind (London)* 308 (1991).
17. Sohn, J. R., and Lunsford, J. H., *J. Mol. Catal.* **32**, 325 (1985).
18. Mizuno, N., and Misono, M., *Chem. Rev.* **98**, 199 (1998).
19. Hill, C. L., and Prosser-McCartha, C. M., *in* "Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds," p. 307. Kluwer Academic, Dordrecht, Norwell, MA, 1993.
20. Neumann, R., and Dahan, M., *Nature* **388**, 353 (1997).
21. Hill, C. L., and Prosser-McCartha, C. M., *Coord. Chem. Rev.* **143**, 407 (1995).
22. Chambers, R. C., and Hill, C. L., *Inorg. Chem.* **28**, 2509 (1989).
23. Hiskia, A., and Papaconstantinou, E., *Inorg. Chem.* **31**, 163 (1992).
24. Ermolenko, L. P., and Giannotti, C., *J. Chem. Soc. Perkin Trans.* 1205 (1996).
25. Duncan, D. C., and Hill, C. L., *J. Am. Chem. Soc.* **119**, 243 (1997).
26. Tanielan, C., Duffy, K., and Jones, A., *J. Phys. Chem. B* **101**, 4276 (1997).
27. Molinari, A., Amadelli, R., Carassiti, V., and Maldotti, A., *Eur. J. Inorg. Chem.* 91 (2000).
28. Molinari, A., Amadelli, R., Andreotti, L., and Maldotti, A., *J. Chem. Soc. Dalton Trans.* 1203 (1999).
29. Subba Rao, Y. V., De Vos, D. E., and Jacobs, P. A., *Angew. Chem. Int. Ed. Engl.* **36**, 2661 (1997).
30. Moller, K., and Bein, T., *Chem. Mater.* **10**, 2950 (1998).
31. Washmon-Kriel, L., Jimenez, V. L., and Balkus, K. J., Jr., *J. Mol. Catal. B* **10**, 453 (2000).
32. Corma, A., and Kumar, D., *in* "Mesoporous Molecular Sieves 1998," Vol. 117, p. 201. Elsevier, Amsterdam, 1998.
33. Shephard, D. S., Maschmeyer, T., Sankar, G., Thomas, J. M., Ozkaya, D., Johnson, B. F. G., Raja, R., Oldroyd, R. D., and Bell, R. G., *Chem. Eur. J.* **4**, 1214 (1998).
34. Xia, Q.-H., Hidajat, K., and Kawi, S., *Chem. Commun.* 2229 (2000).
35. Jun, S., and Ryoo, R., *J. Catal.* **195**, 237 (2000).
36. Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C., and Beck, J. S., *Nature* **359**, 710 (1992).
37. Beck, J. S., Vartuli, J. C., Roth, W. J., Leonowicz, M. E., Kresge, C. T., Schmitt, K. D., Chu, W., Olson, D. H., Sheppard, E. W., McCullen, S. B., Higgins, J. B., and Schlenker, J. L., *J. Am. Chem. Soc.* **114**, 10834 (1992).
38. Inui, T., Kim, J. B., and Seno, M., *Catal. Lett.* **29**, 271 (1995).
39. Shyu, S. G., Cheng, A. W., and Tzou, D. L., *Chem. Commun.* 2337 (1999).
40. Bleloch, A., Johnson, B. F. G., Ley, S. V., Price, A. J., Shepard, D. S., and Thomas, A. W., *Chem. Commun.* 1907 (1999).
41. Maschmeyer, T., Rey, F., Sankar, G., and Thomas, J. M., *Nature* **378**, 159 (1995).
42. Chu, W., Yang, X., Shan, Y., Ye, X., and Wu, Y., *Catal. Lett.* 201 (1996).
43. Khozhevnikov, I. V., Kloetstra, K. R., Sinnema, A., Zandbergen, H. W., and van Bekkum, H., *J. Mol. Catal. A* **114**, 287 (1996).
44. Ghanbari-Siahkali, A., Philippou, A., Dwyer, J., and Anderson, M. W., *Appl. Catal. A* **192**, 57 (2000).
45. Blasco, T., Corma, A., Martinez, A., and Martinez-Escolano, P., *J. Catal.* **177**, 306 (1998).
46. Khenkin, A. M., Neumann, R., Sorokin, A. B., and Tuel, A., *Catal. Lett.* **63**, 189 (1999).
47. Kamada, M., Kominami, H., and Kera, Y. J., *Colloid Interface Sci.* **182**, 297 (1996).
48. Johnson, B. J. S., and Stein, A., *Inorg. Chem.* **40**, 801 (2001).
49. Weissermel, K., and Arpe, H. J., "Industrial Organic Chemistry." VCH, Weinheim, 1997.
50. Schurchardt, U., Cardoso, D., Sercheli, R., Pereira, R., S. da Cruz, R., Guerreiro, M. C., Mandelli, D., Spinace, E. V., and Pires, E. L., *Appl. Catal. A* 211 (2001).
51. Bollbuck, B., Kraft, P., and Tochterman, W., *Tetrahedron* **52**, 4581 (1996).
52. Chemseddine, A., Sanchez, C., Livage, J., Launay, J. P., and Fournier, M., *Inorg. Chem.* **23**, 2609 (1984).
53. Wu, Y., Ye, X., Yang, X., Wang, X., Chu, W., and Hu, Y., *Ind. Eng. Chem. Res.* **35**, 2546 (1996).
54. Fournier, M., Thouvenot, R., and Rocchiccioli-Deltcheff, C., *J. Chem. Soc. Faraday Trans.* **87**, 49 (1991).
55. Ogawa, M., *in* "Annual Reports on the Progress of Chemistry," Vol. 94, p. 209. Royal Society of Chemistry, Cambridge, 1999.
56. Rocchiccioli-Deltcheff, C., Amirouche, M., Che, M., Tatibouet, J. M., and Fournier, M., *J. Catal.* **125**, 292 (1990).
57. Roquerol, F., Roquerol, J., and Sing, K., "Adsorption by Powders and Porous Solids." Academic Press, San Diego, 1999.
58. Von Fuchs, J., Hartl, H., Schiller, W., and Gerlach, U., *Acta Crystallogr. Sect. B* **32**, 740 (1976).
59. Von Fuchs, J., Freiwald, W., and Hartl, H., *Acta Crystallogr.* **34**, 1764 (1978).
60. Whalen, J. W., *J. Phys. Chem.* **66**, 511 (1962).
61. Gilbert, L., and Mercier, C., *in* "Heterogeneous Catalysis and Fine Chemicals III" (M. Guisnet, J. Barbier, J. Barrault, C. Bouchoule, D. Duprez, G. Perot, and C. Montassier, Eds.), p. 51. Elsevier, Amsterdam/New York, 1993.
62. Boarini, P., Carassiti, V., Maldotti, A., and Amadelli, R., *Langmuir* **14**, 2080 (1998).
63. Yamase, T., Takabayashi, N., and Kaji, M., *J. Chem. Soc. Dalton Trans.* 793 (1984).