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Oxidation of geraniol and other substituted olefins with hydrogen peroxide using mesoporous, sol–gel-made tungsten oxide–silica mixed oxide catalysts

Filippo Somma, Giorgio Strukul [*]

Dipartimento di Chimica, Università di Venezia, and Consorzio INSTM, Dorsoduro 2137, 30123 Venezia, Italy

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Abstract

The preparation of a series of mesoporous tungsten oxide–silica mixed oxides by sol–gel methods under basic conditions is reported. Surface modification with methyl and 3-chloropropyl groups is possible in an amount between 10 and 40 mol% with respect to the silane precursor. The amount of polar organic functional groups controls the surface area, the porosity, and the catalytic activity of the solids in the oxidation of different substrates with hydrogen peroxide. The oxidation of geraniol is studied in detail. The catalysts are active and produce epoxides in good yields. The latter are influenced by the presence of polar organic groups. The preparation method allows the preparation of catalysts that are resistant to leaching and can be recycled several times without appreciable loss of activity.

Keywords: Oxidation; Allylic alcohols; Hydrogen peroxide; Sol–gel; WO_3–SiO_2 catalysts

1. Introduction

The oxidation of organic compounds with hydrogen peroxide is very important for environmentally friendly industrial technologies. Hydrogen peroxide is a very attractive oxidant: it is cheap, environmentally clean, and easy to handle, but it is poorly active without a catalyst. Zeolites and crystalline silicate-based systems are active and selective epoxidation catalysts with hydrogen peroxide [1] but their small pore dimensions constitute also their main limitation when relatively large organic molecules are used. In recent years amorphous titania–silica mesoporous materials (aerogels and xerogels) have emerged as promising catalysts with organic hydroperoxides [2].

One of the problems when working with mixed oxides instead of zeolites in the liquid phase is their generally high hydrophilicity, which hampers the diffusion of hydrophobic organics inside the pores of the solid. The possibility of modifying the surface of these systems is an important aspect for improving their adsorption properties with respect to organic reactants [3,4]. Moreover, when metal complex catalysts or metal oxides are immobilized onto silica, the surface hydrophobization with methyl, phenyl, and other groups prevents active metals from leaching when H_2O_2 is used as oxidant [3a,3b].

To date, most of research work in this area has focused on supported TiO_2 as the active phase. Unfortunately, all studies dealt mainly with *t*-butylhydroperoxide as the oxidant, because the activity observed with H_2O_2 was rather modest, mainly because TiO_2 crystallites decompose the oxidant.

We have recently reported some ZrO_2–SiO_2 mesoporous and microporous mixed oxides that have been employed for the oxidation of variety of olefins with hydrogen peroxide, leading mainly to the formation of diols, and show a high efficiency in H_2O_2 use [4].

It is well known that tungsten-based homogeneous catalysts show excellent activity and selectivity in epoxidation reactions with H_2O_2 [5]. On the other hand, examples of

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[*] Corresponding author. Fax: +39 041 234 8517.
E-mail address: strukul@unive.it (G. Strukul).

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supported WO_3 as catalysts for epoxidation reactions with H_2O_2, where the active phase does not dissolve during the reactions, are relatively rare [6,7]. In fact, WO_3 dissolves in hydrogen peroxide solutions to give the so-called “pertungstic acid” that is an excellent soluble epoxidation catalyst [8]. Deng and co-workers [6a,6b] have recently reported a series of WO_3–SiO_2 catalysts made by impregnation of a sol–gel-made silica with ammonium tungstate, in which leaching from the matrix was prevented by calcination at 550 °C. During the use of these materials in the oxidation of cyclopentene to glutaraldehyde with hydrogen peroxide, extensive sintering could be observed (leading to deactivation of the catalyst) that could be reverted by calcination.

In this work we report the preparation and characterization of mesoporous heterogeneous WO_3–SiO_2 catalysts made by sol–gel techniques that allow the incorporation of W in the silica network, thereby preventing the problems described above. These materials are very interesting catalysts for the selective epoxidation of allylic alcohols. In addition, being allylic alcohols moderately hydrophilic molecules, we report also the effect on the activity and selectivity of the surface modification of the catalysts with apolar (methyl) and moderately polar (3-chloropropyl) organic groups that are introduced to improve the accessibility on the active sites to molecules that are so different in terms of hydrophilicity properties such as hydrogen peroxide and an olefin.

2. Experimental

2.1. Materials

The following metal alkoxides were used: tetramethoxysilane (TMOS) and methyltriethoxysilane (MTES), 3-chloropropyltrimethoxysilane (3CPTMES) (both from Aldrich), tungsten hexa-*iso*-propoxide (Chemat Technology inc.). The oxidants was 35% hydrogen peroxide (Fluka). Substrates were purchased from Fluka. All chemicals were purum or puriss grade and used without further treatment.

2.2. Methods

BET surface areas and pore size were determined with N_2 at 77 K on a Micromeritics ASAP 2000 apparatus. X ray powder diffraction analysis was performed using a X’Pert diffractometer operating with Cu-K_α Ni-filtered radiation, a graphite monochromator, and a proportional counter with a pulse height discriminator. The diffraction patterns were measured step by step (0.05° in 2θ). Differential thermal analysis (DTA) was performed on a Netzsch instrument in flowing air with temperature rate set at 10 °C/min in the 25–700 °C temperature range. GC-MS measurements were performed on a Hewlett–Packard 5971 mass-selective detector connected to a Hewlett–Packard 5890 II gas chromatograph. ICM–MS measurements were carried out on a Agilent 7500 instrument.

Table 1
Preparation features of different WO_3–SiO_2 (1% W) catalysts

Sample	Heating temperature (°C)	Amount functional group (%mol)
WO_3–SiO_2-110	110	–
WO_3–SiO_2-200	200	–
WO_3–SiO_2-500	500	–
WO_3–SiO_2-700	700	–
WO_3–SiO_2-10ClPr	110	10
WO_3–SiO_2-20ClPr	110	20
WO_3–SiO_2-30ClPr	110	30
WO_3–SiO_2-20Me	200	20
WO_3–SiO_2-40Me	200	40
WO_3–SiO_2-Aero	200	–

2.3. Preparation of xerogels

The following general preparation procedure was used in all cases. To a 250-ml beaker were added TMOS and MTES or 3CPTMES in the appropriate amount (see Table 1 for composition) when necessary. In a typical experiment 4.7 ml TMOS (or the appropriate silane precursors mixture) were dissolved in 14 ml EtOH. The mixture was stirred at room temperature for 5 min. After this time, 1.05 ml of a 30% ammonia solution was added. Hydrolysis occurred within 5 min. Over the prehydrolyzed mixture, 1.17 ml of a $W(OPr)_6$ solution in propanol (5 g/100 ml) was added, in order to obtain a final composition of 1 wt% W/SiO_2. Gelation was completed in 5 min. Gels were normally transparent and were aged for 72 h at room temperature. The different xerogels were dried at 110 °C overnight. Where necessary the samples were calcined at 200, 500, and 700 °C in air for 2 h: gas flow, 30 ml/min; heating ramp 3 °C/min.

2.4. Preparation of the aerogel

A modified tungsten alkoxide precursor was synthesized according to the procedure reported in Ref. [9]. A solution of acetylacetone (acacH), i-PrOH (3 ml), and $W(OR)_6$ (acac/$W(OR)_6$ 1/1) was refluxed for 1 h under N_2 with stirring. The modified tungsten precursor and TMOS (9.8 ml) were dissolved in i-PrOH (10 ml). A hydrolyzing solution consisting of distilled water (6 ml) and nitric acid (0.27 ml) diluted in i-PrOH (6 ml) was added dropwise to the alkoxides solution under vigorous stirring. After 90 min, 40 ml i-PrOH was introduced to the system. The corresponding molar ratios H_2O/alkoxide/acid were 5/1/0.09. The mixture was transferred to a stainless-steel autoclave.

The conditions for obtaining a supercritical drying of the solvent are: $V_c = 48$ ml; $P_c = 48$ atm; $T_c = 235$ °C. The high-pressure system was flushed with N_2, pressurized to 7 atm, and heated at 240 °C. The autoclave was kept at the final temperature for 60 min to ensure complete thermal equilibration. The final pressure was about 80 atm. The pressure was then released at constant temperature and finally the system was flushed with N_2 and cooled to room temperature. The sample was calcined at 200 °C in air for 2 h: gas flow, 30 cc/min; heating ramp 3 °C/min.

A summary of the preparation parameters is reported in Table 1.

2.5. Catalytic oxidation procedures

Catalytic reactions were performed in 10-ml glass vials equipped with a small magnetic bar. The catalyst (10 mg), substrate (1 mmol), and H_2O_2 (1 mmol) were placed in the vial under N_2 flow. The reaction vessels were sealed and placed in an oil bath at constant temperature, while an external magnetic stirrer ensured agitation. At different reaction times the mixtures were cooled down to room temperature, diluted with MeOH (2 ml), and analyzed by GC. Product identification was performed by GC-MS analysis and by comparison with authentic samples. Conversions and selectivities were determined by analysis of the relative peak areas of reactants and products. Residual H_2O_2 was determined by iodometric titration.

Leaching of W was determined in randomly selected catalytic runs by analyzing the reaction solution with ICP-MS technique.

3. Results and discussion

3.1. Preparation

All xerogels were prepared via a sol–gel method under basic conditions. Under the conditions reported under Experimental, gelation for the individual oxides occurs in 4–5 min. The simultaneous introduction of W precursor and the silica precursors is not possible because of the very different gelation rates that would lead to segregation of WO_3 in the silica matrix. This problem was solved by adding the W precursor in the prehydrolyzed silicon alkoxide solution. This is an important point for the achievement of mixed oxides with high homogeneity and regular dilution of W centers within the silica matrix. The preparation of highly transparent homogeneous gels is generally a good indication of a high W dispersion, which is a key step for stabilizing the catalyst against leaching.

All gels were aged in air for 72 h to yield vitreous xerogels. They were subsequently dried in the oven at 110 °C overnight to eliminate organic and inorganic solvents.

In the preparation of the aerogel sample, the preparation mixture was introduced into the autoclave without any apparent gelation. In this case, supercritical solvent evaporation is a fundamental step for obtaining a transparent gel.

All samples that did not contain surface organic groups were also calcined at different temperature (200, 500, 700 °C).

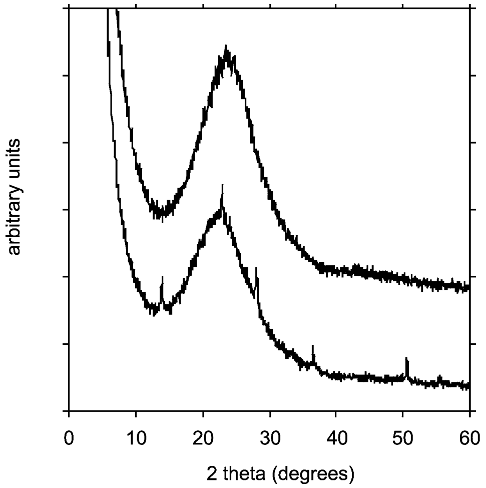


Fig. 1. Powder X-ray diffraction profiles for WO_3–SiO_2-500 (upper) and WO_3–SiO_2-Aero (lower).

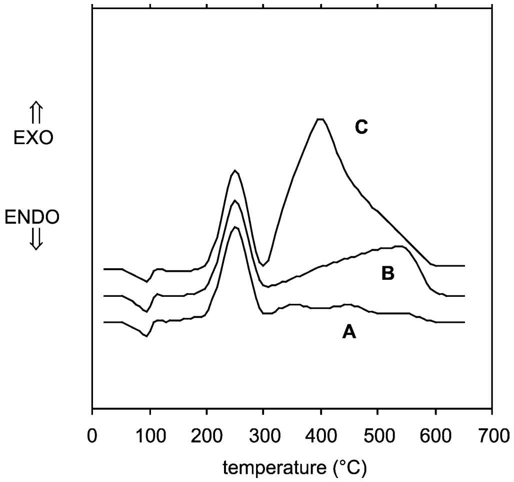


Fig. 2. Typical DTA analyses for some representative samples: A, WO_3–SiO_2-500; B, WO_3–SiO_2-40Me; C, WO_3–SiO_2-30ClPr.

3.2. Characterization

X-ray powder diffraction analysis indicated that all xerogels were completely amorphous, even those calcined at 700 °C, a feature that is a reasonable indication that WO_3 is well dispersed in the silica matrix [3a,3b]. On the contrary, the aerogel sample showed the presence of hexagonal WO_3 (peaks at 14°, 23°, 28°, 36°, 51°, and 56° in 2θ) in the amorphous matrix of silica (Fig. 1). This is a clear indication that the low amount of W (1%) is not a limitation to detection, if the WO_3 phase is crystalline.

Some DTA profiles are shown in Fig. 2. For each sample we can roughly divide the explored temperature range into two regions. The first one, from 50 to 250 °C, is dominated by an exothermic, broad peak, most likely due to loss of organic solvents; Fig. 2 indicates also that there are no significant differences among the various samples. The second region ranges from 250–300 °C to 600 °C and is dominated by an exothermic band only in the case of the

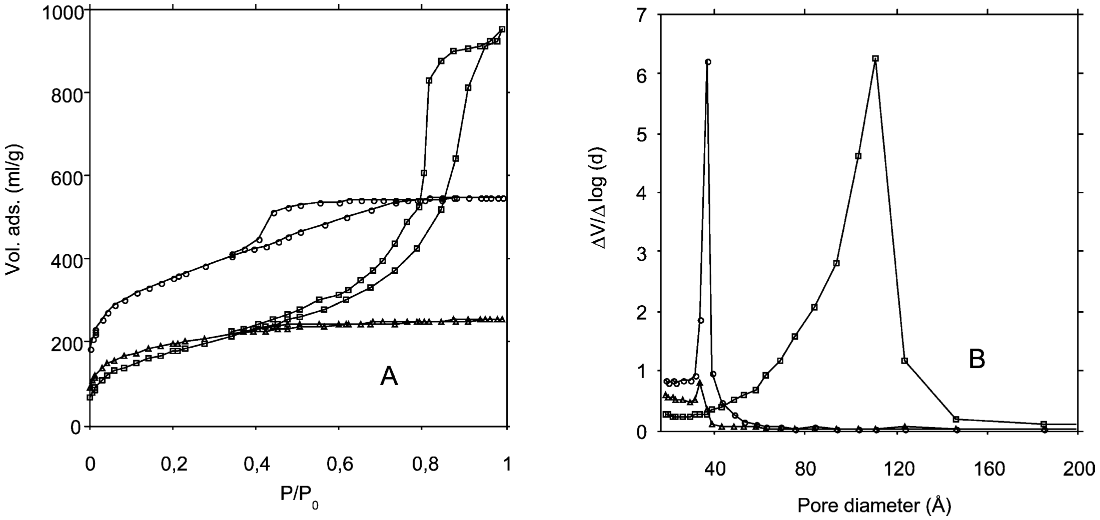


Fig. 3. (A) N_2 adsorption isotherms for some representative samples; (B) BJH pore-size distributions for some representative samples. (○) WO_3–SiO_2-500; (□) WO_3–SiO_2-40Me; (△) WO_3–SiO_2-30ClPr.

Table 2
Surface area and average pore diameter for different WO_3–SiO_2 samples

Sample	Heating temperature (°C)	BET surface area (m^2/g)	BJH average pore diameter (Å)
WO_3–SiO_2-110	110	550	41
WO_3–SiO_2-200	200	820	41
WO_3–SiO_2-500	500	528	41
WO_3–SiO_2-700	700	540	40
WO_3–SiO_2-10ClPr[a]	110	511	38
WO_3–SiO_2-20ClPr[a]	110	373	37
WO_3–SiO_2-30ClPr[a]	110	113	42
WO_3–SiO_2-20Me	200	830	53
WO_3–SiO_2-40Me	200	661	108
WO_3–SiO_2-Aero	200	1434	206

[a] For these samples only the diameter of the residual fraction of mesopores is shown.

surface-modified samples; the latter band is most likely due to decomposition of the surface organic groups. Interestingly, the nonmodified sample (curve A) does not show any evidence of the exothermic peak at ~ 600 °C found by Deng and co-workers in their samples [6a] and attributed to the amorphous/crystalline transition.

Surface area and pore-size distribution were determined from N_2 adsorption/desorption isotherms and some typical ones are shown in Fig. 3A. Those of the nonsurface-modified and methyl-modified samples are type IV isotherms according to IUPAC [10] and they show a hysteresis loop typical of mesoporous solids. On the contrary, the chloropropyl-modified samples are extensively microporous. Fig. 3B shows also some typical pore size distributions for surface-modified and nonmodified WO_3-containing xerogels. This is generally rather narrow and falls into the range of mesopores.

The BET [11] surface areas of the samples, along with their average pore diameter calculated according to BJH method [12] are reported in Table 2. We will now distinguish between modified and nonmodified samples. An increase of the chloropropyl content increases the amount of micropores (in Fig. 3B sample WO_3–SiO_2-30ClPr is shown, i.e., the most microporous), while an increase of methylation degree gives the opposite effect and the isotherm shifts the hysteresis loop toward larger P/P_0 values (in Fig. 2A WO_3–SiO_2-40Me is shown). Also the aerogel sample showed an isotherm typical of mesoporous materials. However, its pore-size dimensions, while still in the range of mesopores, show a very large distribution (50–800 Å).

As can be seen from Table 2, in the 3-Cl-propyl-modified samples the overall surface area is strongly dependent on the amount of organic functional groups. On the other hand, their presence does not change the diameter of residual mesopores (the only ones that can be revealed by the BJH method), but decreases their amount. Fig. 3B shows that at 30% chloropropylation the amount of residual mesopores is drastically decreased. Conversely, the presence of methyl groups increases greatly the average pore diameter (41 to 108 Å) while at the same time decreasing the surface area (820 to 661 m^2/g).

The calcination temperature does not modify the average pore diameter but shows a high influence on the surface area. As can be seen from Table 2 there is a maximum for calcination at 200 °C. Indeed a surface area of ~ 800 m^2/g is not surprising for sol–gel silicas calcined at low temperatures [13] and it is conceivable that it should be probably even higher for WO_3–SiO_2-110. However, in view of the DTA analysis reported in Fig. 2, the lower value observed for WO_3–SiO_2-110 could be due to a less effective surface solvent removal at 110 °C. The decrease in surface area observed for samples calcined at higher temperatures is just a normal effect due to surface hydroxyls condensation. Similar effects have been previously observed in ZrO_2–SiO_2 mixed oxides prepared by sol–gel methods [4a]. On the same DTA

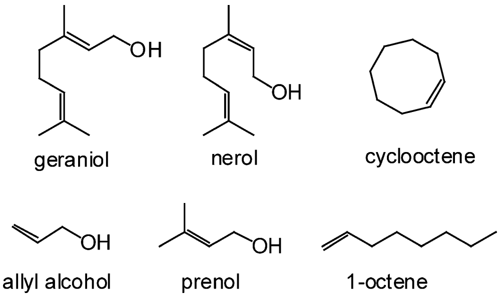
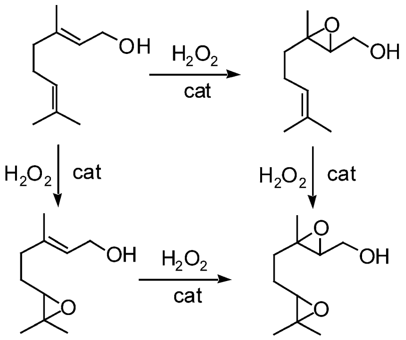


Chart 1.



Scheme 1.

basis, calcination of the surface-modified samples at temperatures higher than 200 °C is not recommended.

3.3. Oxidation of geraniol

The oxidation of geraniol (Chart 1) with 35% hydrogen peroxide was chosen as the reference reaction to compare the behavior of the different catalysts. Geraniol shows interesting properties, as it has two different double bonds: one is in allylic position with respect to the –OH group, while the other one (the 6–7 double bond) is isolated. In principle, different epoxidation products can be observed (see Scheme 1), all giving the corresponding diols upon hydrolysis. In all cases we have observed only the oxidation of the 2–3 double bond with the formation of the corresponding epoxyalcohol and the subsequent ring opening due to hydrolysis and formation of the corresponding diol. This behavior is typical for tungsten and titanium chemistry [14,15], where the –OH functionality is known to coordinate to the transition metal center and olefin epoxidation occurs preferentially at the allylic position. The reaction was carried out in the absence of solvent, a condition that may be of interest with respect to environmental issues.

Table 3
Reactivity of different WO_3–SiO_2 catalysts in the oxidation of geraniol with hydrogen peroxide

Entry	Sample	Conversion (%)		Selectivity epoxide (%)	Spec. conversion (%/m^2)
		Geraniol	H_2O_2		
1	WO_3–SiO_2-110	69	83	18	0.125
2	WO_3–SiO_2-200	61	100	90	0.074
3	WO_3–SiO_2-500	68	100	94	0.128
4	WO_3–SiO_2-700	79	100	80	0.146
5	WO_3–SiO_2-10ClPr	60	95	31	0.117
6	WO_3–SiO_2-20ClPr	61	95	44	0.163
7	WO_3–SiO_2-30ClPr	57	90	52	0.504
8	WO_3–SiO_2-20Me	81	92	88	0.097
9	WO_3–SiO_2-40Me	64	75	55	0.092
10	WO_3–SiO_2-Aero	64	90	92	0.044

Reaction conditions: catalyst, 10 mg; geraniol, 1 mmol; 35% H_2O_2, 1 mmol; temperature, 70 °C; reaction time, 210 min.

Initial tests were carried out on plain WO_3–SiO_2 samples at 70 °C. In all cases reaction products were only the epoxyalcohol and the corresponding diol (actually a triol); no other products were observed. The catalysts calcined at the different temperatures were tested. In Table 3 their conversions after 210 min, the selectivity to epoxide, and hydrogen peroxide consumption are reported. Conversion vs time profiles are shown in Fig. 4A. As can be seen an increase

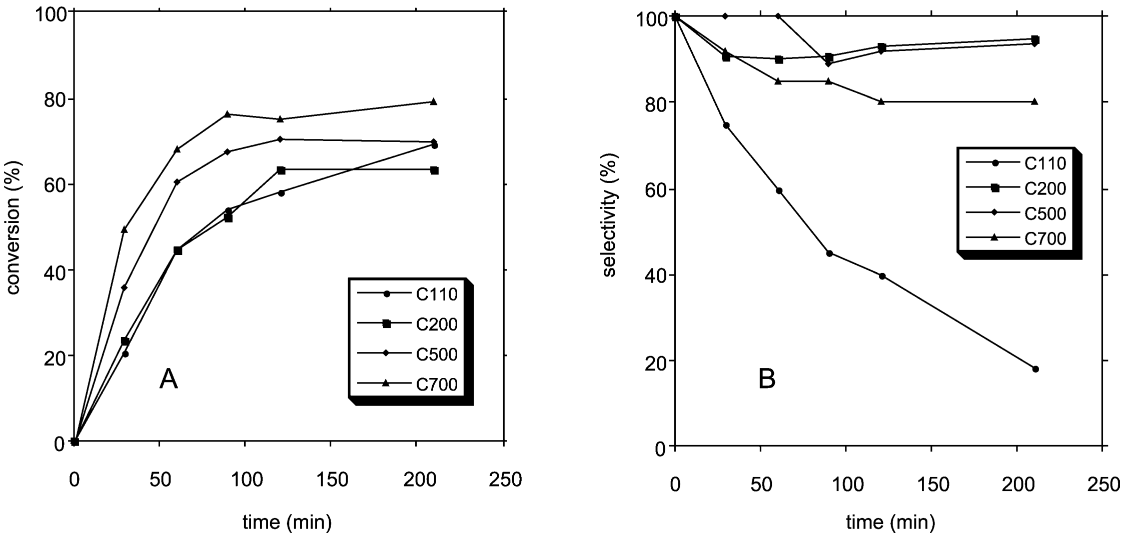


Fig. 4. (A) Conversion vs time plots for the oxidation of geraniol with hydrogen peroxide catalyzed by samples calcined at different temperatures. (B) Selectivity to epoxide vs time plots for the oxidation of geraniol with hydrogen peroxide catalyzed by samples calcined at different temperatures.

in the initial rate with increasing calcination temperature is observed, while from Table 3 it appears that there is also a moderate tendency to increase the conversion. This is evident also if one considers the specific conversion calculated per square meter of surface, a parameter that is more indicative of the intrinsic catalytic properties of each sample. Sample WO_3–SiO_2-110 is odd in this respect, as is indicated by both Fig. 4A and Table 3. Again with the exception of WO_3–SiO_2-110, in all cases the maximum conversion occurs after about 120–130 min, while after this time the reaction is practically finished as indicated by the full consumption of H_2O_2. The change in selectivity to epoxide with time is shown in Fig. 4B. As can be seen, in samples calcined at 200 °C or above, a moderate decrease within the first 100 min is observed and then the selectivity stabilizes in the range 80–95%. The sample dried at 110 °C is again an exception as the selectivity to epoxide decreases constantly and after 210 min it is as low as 18% (Fig. 4B and Table 3). The anomalous behavior of this sample in all respects could probably be due to incomplete drying at 110 °C.

The presence of 3-Cl-propyl groups on the surface does not result in significant improvements on the activity and hydrogen peroxide consumption, if compared to the corresponding nonmodified sample (i.e., WO_3–SiO_2-110). Moreover, an increase in the 3-Cl-propyl content does not seem to have any influence on the conversion and hydrogen peroxide consumption (Table 3). Conversely, an analysis of the specific conversion indicates a significant improvement as the chloropropyl content increases (Table 3, entries 5–7), as does the selectivity to epoxide which increases from 31 to 52%. Although the effect is moderate, it is in line with previous findings on the oxidation of olefins with ZrO_2–SiO_2 modified with methyl groups [4a] and is indicative of a more favorable environment for the reaction to take place.

If we now compare the behavior of the two methylated samples with the corresponding unpromoted sample (Table 3, entries 2, 8, and 9), it is clear that an improvement in activity and selectivity can be achieved only at a moderate methylation degree (20%, entry 8). The specific conversion is practically similar in both methylated samples.

Overall, the results obtained in the epoxidation of geraniol seem to show that only a moderate hydrophilicity of the surface is beneficial to achieve good conversions and selectivities. These catalyst surface conditions can be better achieved either by chloropropylation or by simple calcination. Indeed, 30% chloropropylation leads to higher specific conversions but at the expenses of a drop in surface area and a lower selectivity to epoxide. This observation partly differs from the previous findings obtained with simple olefins [4], but is in line with the moderate hydrophilicity of the substrate which contains a –OH functional group. Therefore, the general principle that “like adsorbs like” seems to hold even in this case, at least in qualitative terms.

Table 4
Effect of catalyst recycling in the oxidation of geraniol with hydrogen peroxide catalyzed by WO_3–SiO_2-700

Recycle	Conversion (%)	Epoxide selectivity (%)
Fresh	71	81
First	70	91
Second	71	89
Third	70	94

Reaction conditions: catalyst, 10 mg; geraniol, 1 mmol; 35% H_2O_2, 1 mmol; temperature, 70 °C; reaction time, 120 min.

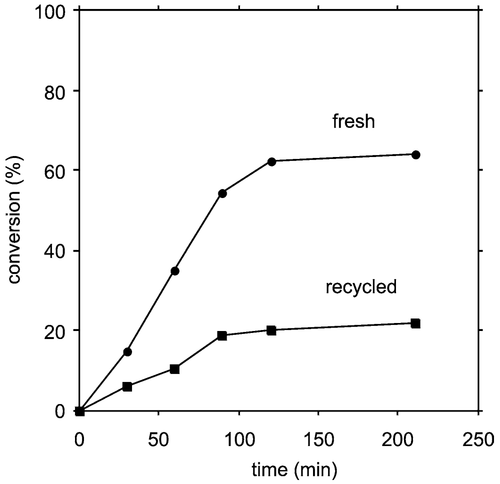


Fig. 5. Effect of WO_3–SiO_2-Aero catalyst recycling on the oxidation of geraniol with hydrogen peroxide.

Some tests to check the dissolution of WO_3 into the reaction medium were carried out on some randomly selected reaction mixtures after a 210-min reaction time. The catalyst was filtered and new reagents were added to the solution. The activity observed was negligible (1–2% conversion after 60 min) and this was confirmed also by ICP-MS analysis that revealed only 2–3 ppm of W in the solution after filtration.

3.4. Catalyst recycling

Tests on catalyst recycling were carried out on WO_3–SiO_2-700. The oxidation of geraniol was tested with a fresh sample followed by a series of recycling using the solid isolated from the previous reaction mixture by simple centrifugation. The recovered solid was dried for 5 h in the oven at 110 °C and reused. A summary of the results obtained in the different cycles is collected in Table 4. As can be seen, after 4 cycles there is no loss of activity (conversion), while the selectivity to epoxide seems to benefit to some extent from recycling.

A comparison with the aerogel sample (WO_3–SiO_2-Aero) seems interesting. From Table 3, it appears that this catalyst (entry 10) shows comparable catalytic performance with the other nonmodified samples, but it loses very much

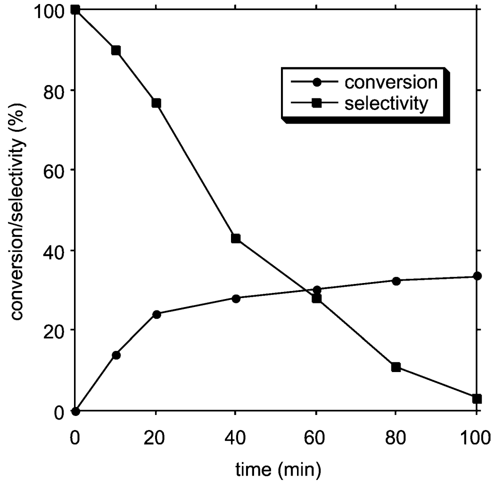


Fig. 6. Conversion/selectivity to epoxide vs time plots in the oxidation of prenol with hydrogen peroxide using WO_3–SiO_2-700 as catalyst.

in activity upon recycling (Fig. 5). This corresponds to a significant loss of tungsten (∼ 60%) during the first cycle. Leaching of W is probably due to the presence of crystalline WO_3 in the structure as shown by XRD analysis (Fig. 1).

This result seems to support the idea that leaching can be avoided only when the active component is well dispersed and tightly held within the matrix. This is also in agreement with the findings of Deng and co-workers [6a,6b] who observed catalytic activity only when WO_3 is amorphous and well dispersed. It should be pointed out that the catalysts used by the latter authors were prepared by simple impregnation of Na_2WO_4 on silica and calcined at 550 °C or above. This procedure prevents tungsten from leaching, but leads to sintering of the amorphous WO_3 particles during catalyst use. This behavior was evident especially upon catalyst recycling. This leads to a loss of activity and selectivity that could be reverted by recalcination of the catalyst at 550 °C [6a]. The preparation method reported in the present paper seems to give more stable catalysts as WO_3 entities are covalently bound to the support. In this way they can neither dissolve in the reaction medium nor migrate to form larger clusters.

3.5. *Oxidation of other olefins*

Other allylic alcohols (nerol, prenol, allyl alcohol) and simple olefins (cyclooctene and 1-octene, all shown in Chart 1) were tested in the oxidation with hydrogen peroxide. The catalysts chosen were WO_3–SiO_2-700 because of its good results shown in the epoxidation of geraniol, the chloromethylated samples because of the effect shown on the selectivity, and the methylated samples, only in the case of the most hydrophobic substrates (cyclooctene and 1-octene). Results are summarized in Table 5. Allyl alcohol and 1-octene gave no conversion under the usual experimental conditions.

Table 5
Oxidation of allylic alcohols and olefins with hydrogen peroxide using different WO_3–SiO_2 catalysts

Sample	Substrate	Reaction time (min)	Conversion (%)	Epoxide selectivity (%)	Spec. conversion (%/m^2)
WO_3–SiO_2-700	Nerol	120	63	84	0.117
WO_3–SiO_2-10ClPr	Nerol	210	60	30	0.117
WO_3–SiO_2-20ClPr	Nerol	210	53	32	0.142
WO_3–SiO_2-30ClPr	Nerol	210	55	40	0.487
WO_3–SiO_2-110	Prenol	60	47	73	0.085
WO_3–SiO_2-700	Prenol	40	28	43	0.052
WO_3–SiO_2-10ClPr	Prenol	60	37	71	0.072
WO_3–SiO_2-20ClPr	Prenol	60	34	56	0.091
WO_3–SiO_2-30ClPr	Prenol	60	36	37	0.318
WO_3–SiO_2-700	Cyclooctene	8	3	100	0.005
WO_3–SiO_2-10ClPr	Cyclooctene	8	4	100	0.008
WO_3–SiO_2-20ClPr	Cyclooctene	8	8	100	0.021
WO_3–SiO_2-30ClPr	Cyclooctene	8	15	100	0.133
WO_3–SiO_2-20Me	Cyclooctene	8	6	100	0.007
WO_3–SiO_2-40Me	Cyclooctene	8	14	100	0.021

Reaction conditions: catalyst, 10 mg; substrate, 1 mmol; H_2O_2, 1 mmol; reaction time, 120 min. Temperatures: nerol and cyclooctene, 70 °C; prenol, 40 °C.

The epoxidation of nerol showed similar results with respect to geraniol. No significant effects could be attributed to the different structures of the two isomeric substrates.

The oxidation of prenol was carried out at a lower temperature (40 °C) and for shorter times with respect to the other allylic alcohols, because the selectivity to epoxide drops quite dramatically with time (Fig. 6). After 80–100 min the corresponding glycol is practically the only product observed. The effect on selectivity is very similar to the one shown in Fig. 4B for WO_3–SiO_2-110. Interestingly in this case, the latter catalyst seems to be more selective than WO_3–SiO_2-700, i.e., the opposite of what was observed with geraniol. Also odd is the effect of chloropropylation on the selectivity: While with geraniol or nerol an increase in chloropropyl groups content increases the selectivity to epoxide, with prenol the opposite occurs (Table 5). A possible rationale for this behavior might be found in the different structure of the allylic alcohols; i.e., prenol does not have a long aliphatic chain and therefore is less hydrophobic than geraniol or nerol. This might explain why better results are observed with the least hydrophobic catalyst surface, i.e., WO_3–SiO_2-110. The lack of reactivity with allyl alcohol could be simply due to the fact that the absence of alkyl substituents at the C=C double bond makes it too electron poor (insufficiently activated) for the reaction to proceed. This result, as well as the lack of activity toward 1-octene, is in line with the well-known behavior observed in the oxidation with W(VI) complexes and, more generally, d^0 transition metal peroxo complexes in solution [16]. In this case, the metal-centered transformation consists in the nucleophilic attack of the olefin onto an electron-poor peroxy oxygen formed by interaction of the oxidant with the d^0 transition metal center. Support for this view is provided by the nature of the epoxy alcohols obtained from geraniol and nerol. As indicated by Chart 1, the latter substrates are isomers and the corresponding epoxides are also isomers. A metal-centered oxidation similar to that observed with soluble species should lead, with either substrate, to the formation of a single epoxide isomer, not to a mixture of both as observed with a radical-type mechanism. This is indeed the case as the *trans* olefin (geraniol) gives the *trans* epoxide, while the *cis* olefin (nerol) gives the *cis* epoxide.

In the oxidation of cyclooctene, epoxide is the only product. This is no surprise as cyclooctene epoxide is quite stable to hydrolysis. Although conversions are very low, the influence of the functional groups (3-Cl-propyl and methyl) is clear and similar to previous observations with surface-modified ZrO_2–SiO_2 samples [4a].

4. Conclusions

The results reported in this work clearly show that sol–gel preparation methods are a viable way of preparing mesoporous WO_3–SiO_2 mixed oxides with controlled morphological properties and these samples are indeed effective catalysts for the selective oxidation of allylic alcohols with hydrogen peroxide to give the corresponding epoxides. Reactions can be conveniently carried out in the absence of solvent and this is in principle more environmentally acceptable and potentially attractive for practical use.

Surface modification and drying conditions are the key parameters for controlling the morphology of the catalysts and the surface hydrophilicity properties. The extent of chloropropylation or the calcination temperature plays an important role in increasing the selectivity to epoxide and, to some extent, the activity of the catalysts.

Catalysts can be recycled several times with no loss of activity and some benefits with respect to epoxide selectivity. These properties are related to the preparation method which allows the formation of amorphous WO_3 entities, well dispersed and tightly held within the silica matrix. This ensures the formation of materials that are very stable both against leaching and against sintering under catalytic conditions, with no need for reactivation.

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