

Communication

Application of Hydrogen Peroxide Encapsulated in Silica Xerogels to Oxidation Reactions

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Abstract: Hydrogen peroxide was encapsulated into a silica xerogel matrix by the sol-gel technique. The composite was tested as an oxidizing agent both under conventional and microwave conditions in a few model reactions: Noyori's method of octanal and 2-octanol oxidation and cyclooctene epoxidation in a 1,1,1-trifluoroethanol/ Na_2WO_4 system. The results were compared with yields obtained for reactions with 30% H_2O_2 and urea-hydrogen peroxide (UHP) as oxidizing agents. It was found that the composite has activity similar to 30% H_2O_2 and has a several advantages over UHP such as the fact that silica and H_2O are the only products of the composite decomposition or no contamination by urea or its derivatives occurs; the xerogel is easier to heated by microwave irradiation than UHP and could be used as both an oxidizing agent and as solid support for microwave assisted solvent-free oxidations.

Keywords: oxidation; epoxidation; microwave irradiation; silica xerogel; hydrogen peroxide; sol-gel; fluoroalcohols; urea-hydrogen peroxide

1. Introduction

One of the methods for the preparation of porous materials is sol-gel processing [1]. The method is characterized by the formation of stable colloidal solutions (sol) in the first step followed by anisotropic condensation of colloidal particles producing a polymeric network with an entrapped solution. After washing and removal of the solvent xero- or aerogels are formed depending on the

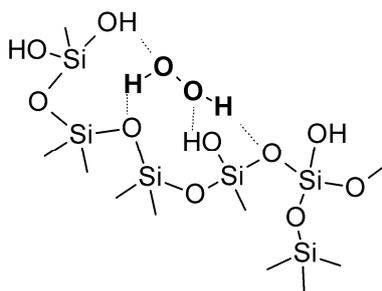
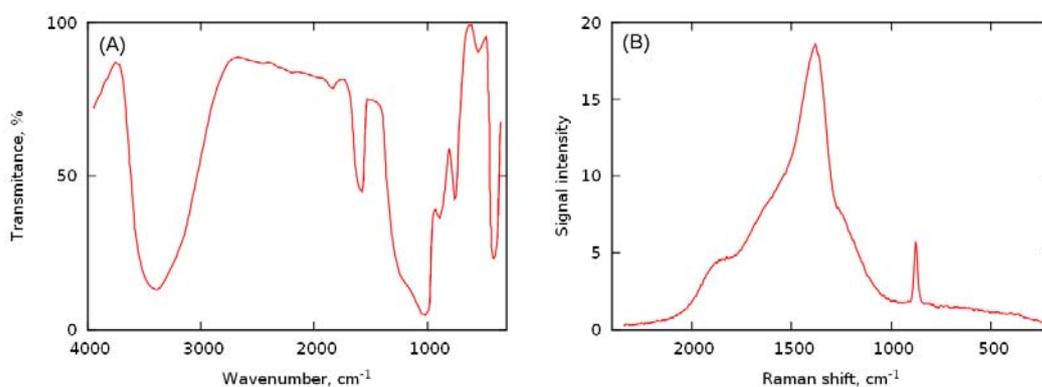
drying mode. The sol-gel technique is employed for the production of porous solids, such as silica and alumina, widely used as catalyst supports. Various metal substituted silica matrices were synthesized and catalytic activity in oxidation reactions was demonstrated. For example titania-silica xerogels and aerogels were used as a catalyst for oxidation reactions with H_2O_2 or *tert*-butyl hydroperoxide as oxidants [2]. The oxidation of some arenes with alkyl side groups by H_2O_2 with tungstoboric acid supported on SiO_2 xerogels was reported [3]. Additionally, a xerogel composite of V_2O_5 was evaluated as a catalyst for the epoxidation of styrene and cyclooctene using iodobenzene, H_2O_2 and *m*-chloro-perbenzoic acid as oxidants [4]. Metallosilicate compounds, prepared by dispersion of metal oxide (TiO_2 , MoO_3 or WO_3) in amorphous silica, were catalytically active in the oxidation of alkenes and alcohols with 30% H_2O_2 solution [5].

Sol-gel processed porous silica glasses also have considerable potential as carriers for controlled drug and temperature-sensitive molecule release [6]. Recently, a sol-gel method was successfully applied for incorporation of H_2O_2 into a silica xerogel matrix to obtain a new antimicrobial composite for medical applications [7]. It was demonstrated that the xerogel was biologically active to nearly the same extent as H_2O_2 solutions [7]. The composite containing up to 68% of H_2O_2 was stable because of the formation of strong hydrogen bonds between siloxane oxygens and H_2O_2 [7,8]. The studies have shown that H_2O_2 was quickly and fully released from the composite into water [7].

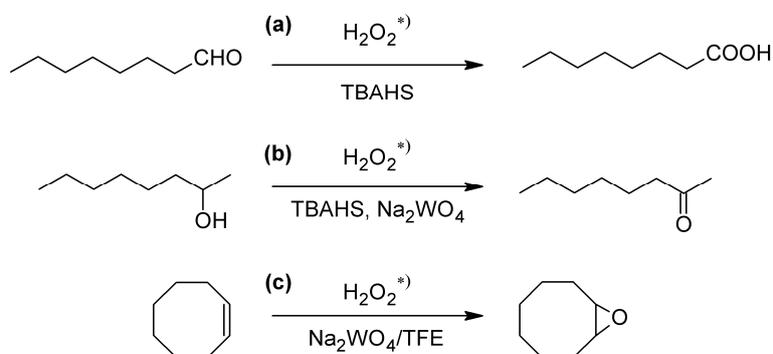
To the best of our knowledge, silica xerogel- H_2O_2 composites have not been used in organic synthesis as an oxidant. This paper demonstrates a successful application of these xerogels as a H_2O_2 source for the oxidation of aldehydes, secondary alcohols and epoxidation of cycloolefins, under both conventional and microwave conditions.

2. Results and Discussion

Drying of a mixture of H_2O_2 in silicic acid sol results in the evaporation of H_2O and partially of H_2O_2 . Simultaneously, silicic acid undergoes condensation and polymerization (crosslinking) followed by an aggregation. Further drying caused the transformation of the silica gel into a silica xerogel and entrapment of both H_2O and H_2O_2 inside the silica network (Figure 1). The IR spectrum (Figure 2A) of the composite is similar to described in the literature [8] and shows characteristic peaks of hydrated silica (broad band $3700\text{--}3000\text{ cm}^{-1}$ O–H stretching frequencies, 1630 cm^{-1} molecular bending vibrations of water, $1400\text{--}1000\text{ cm}^{-1}$ deformation vibrations of the hydroxyl of Si–OH) and H_2O_2 (1350 cm^{-1} H–O–O bending band). Additionally, the Raman spectrum [Figure 2B] shows a peak at 876 cm^{-1} clearly indicating presence of the peroxide. The amount of encapsulated H_2O_2 and the mass ratio of $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ depend on drying time and temperature, which was monitored by weighing the composite during drying [7]. The determined average composition of the obtained composites was 40% H_2O_2 , 43% H_2O and 17% SiO_2 . It was found that loading efficiency of H_2O_2 was c.a. 50%, thus half of the initial amount of H_2O_2 in a sol was encapsulated in the final product and the rest was lost during drying of the sol.

Figure 1. A simplified structure of silica xerogel-hydrogen peroxide composite [7,8].**Figure 2.** Spectroscopic characterization of silica xerogel-hydrogen peroxide composite: (A) FTIR spectrum, (B) Raman spectrum.

To investigate the activity of H₂O₂ encapsulated in silica xerogel, some model reactions were examined such as Noyori's procedures for solvent-free aldehyde [9] and alcohol [10,11] oxidation and epoxidation of cyclic olefins in fluorinated alcohol as a solvent [12] (Scheme 1). For comparison the reactions were also carried out with 30% H₂O₂ solution and urea-hydrogen peroxide adduct (UHP) as oxidant. Additionally, microwave irradiation was employed to shorten the reaction times and to increase their yields.

Scheme 1. The model reactions: oxidation of octanal (a), 2-octanol (b) and epoxidation of cyclooctene (c).

^{*}) H₂O₂ sources: 30% H₂O₂, UHP or silica xerogel-H₂O₂

The oxidation of octanal (Table 1) both by the 30% of H₂O₂ and H₂O₂ encapsulated in the xerogel gave very good yield of the acid (>80%). Application of UHP resulted in lower conversion of octanal (49%) and, additionally, under microwave condition side reactions took place—most probably condensation of urea with the aldehyde [14]. For that reason, in spite of high conversion, the reaction product was not detected by GC.

Table 1. Effect of a source of H₂O₂ on the oxidation of octanal under conventional and microwaves conditions.

H ₂ O ₂ source	Yield of octanoic acid, %	
	Conventional conditions, 90 °C, 120 min	Microwave irradiation, 90–95 °C, 45 min
30% H ₂ O ₂	86	81
UHP	49	0 ^a
The xerogel	83	73

^a Several undefined by-products were detected by GC and the product (octanoic acid) was not affirmed.

2-Octanol was successfully oxidized in nearly quantitative yield both by the composite and 30% aqueous H₂O₂ (Table 2). The application of UHP as an oxidant lowers the yield of the reaction to 69%. Moreover, when the reaction temperature was decreased to 70 °C, UHP exhibited low reactivity manifested only 6% yield of 2-octanone with comparison to 64% and 56% for aqueous H₂O₂ and the xerogel, respectively. Oxidation under microwave conditions gave very good results only when 30% H₂O₂ was applied.

Table 2. Effect of the source of H₂O₂ on the oxidation of 2-octanol under conventional and microwaves conditions.

H ₂ O ₂ source	Yield of 2-octanone, %	
	Conventional conditions, 80 °C, 30 min	Microwave irradiation, 80–90 °C, 15 min
30% H ₂ O ₂	92 (64 ^a)	99
UHP	69 (6 ^a)	<1
The xerogel	98 (56 ^a)	46

^a Reactions carried out at 70 °C (below melting point of UHP).

In further studies, the yield of cyclooctene oxide was highest for reaction with UHP (94%) as an oxidant, while slightly lower yield (88%) was observed for reactions with 30% H₂O₂. However, in the presence of the xerogel, 58% conversion of the olefine was observed. Elongation of the reaction time or increasing the amount of the xerogel improved the yield.

Table 3. Effect of the source of H₂O₂ on the epoxidation of cyclooctene under conventional and microwaves conditions.

H ₂ O ₂ source	Yield of cyclooctene oxide, %	
	Conventional conditions, 3 h 60 °C	Microwave irradiation, 1 h 60–70 °C
30% H ₂ O ₂	88	90
UHP	94	95
The xerogel	58 (69 ^a , 74 ^b)	71

^a Reaction time was 4 h. ^b Highest amount of the xerogel was used (equal 14 mmol H₂O₂).

Silica xerogel–hydrogen peroxide composites stabilized by addition of small amounts of H₃PO₄ can be stored at 3 °C for 2 months without significant loss of H₂O₂ [7]. However, we have used unstabilized composites. We have found that after 2 weeks of storing at 5 °C, the composite loses about a half amount of H₂O₂ probably because slow decomposition of H₂O₂ catalyzed by heavy metals impurities presented in the silica matrix (probably, traces of Fe²⁺ from “water glass”). Relative instability of the composite could be a reason of its activity in oxidation reactions. In contrast, UHP is a stable H₂O₂ complex and such a high stability could be considered, to be a drawback to its potential chemical reactivity. An oxidation yield might be higher if dissociation of the adduct, *i.e.*, dissolving or melting (m.p. 82 °C [15]) took place. UHP/hexafluoro-2-propanol (HFIP) system was investigated in epoxidation of olefins, and it was concluded that the fluoroalcohol has the unique ability to combine the two requirements: dissociation (dissolving) of the UHP adduct and activation of H₂O₂ [16]. We have observed similar effect of TFE on the epoxidation yield of cyclooctene with UHP as an oxidant (Table 3). The temperature effect on UHP and the silica xerogel–H₂O₂ composite activity was investigated in 2-octanol oxidation (Table 2). At the temperature 70 °C (below melting point of UHP) a conversion of the alcohol was very low and was significantly increased when the temperature risen to 80 °C. In opposition, oxidation with 30% H₂O₂ and also with the composite did not show such high yield–temperature dependency.

We have found that silica xerogel–H₂O₂ composite is more suitable oxidant to microwave assisted reactions than UHP. The composite is easily heated by microwave irradiation probably because they contain c.a. 80% of polar components: H₂O₂ and H₂O. These molecules are relatively weakly bonded to silica matrix and can undergo reorientation in microwave field, resulting in heat generation. Silica matrix is almost transparent for microwave irradiation ($\epsilon'' < 0.001$ 2.5 GHz [17]) and does not heated directly by the radiation. For this reason, undesired superheating effect of the xerogel under microwave condition is much less probably than for solids strongly interacted with microwaves such as chromium dioxide (Magtrieve™) [18]. UHP is a crystalline complex formed by hydrogen bonding between urea and H₂O₂ [15], thus the molecules are locked together in a crystal structure. From that reason solid UHP weakly interacts with microwave irradiation in contrast to the melted one, which strongly absorbs microwave energy. It could cause overheating, thermal decomposition of H₂O₂ and even thermal degradation of urea. This might explain rather poor yields of reactions conducted under microwave condition where UHP were used as an oxidant in the solid state (Tables 1 and 2). A presence of polar solvent could overcome mentioned limitations, e.g., high yields of oxidation with UHP in methanol [19] or 1,4-dioxane-water [20] were obtained in microwave assisted reactions.

H_2O_2 encapsulated in silica matrix shown similar activity in the investigated oxidation reactions as 30% H_2O_2 (Tables 1 and 2). However, the composite exhibited lower activity in epoxidation of cyclooctene carried out in TFE (Table 3), an elongation of the reaction time or increasing of the composite amount improves the yield. On the other hand, fluorous alcohols were found to be excellent activators of H_2O_2 and a several mechanisms based on formation of hydrogen bonds between fluorine and H-O-O hydrogen atom were proposed to explain the phenomenon of the H_2O_2 activation [16,21–25]. Additional, hydrogen bonds found to be responsible for stability of H_2O_2 -silica xerogels. FTIR studies and DFT and B3LYP calculations shown that there are complex interactions between H_2O_2 , H_2O and silica network because of hydrogen bonds formation [8]. It may be possible that H_2O_2 molecules involved in formation of silica complex are not activated by TFE. This might be a reason of the small decrease of the yield of the epoxidation carried out in TFE with silica xerogel– H_2O_2 composite with comparison to 30% H_2O_2 or UHP.

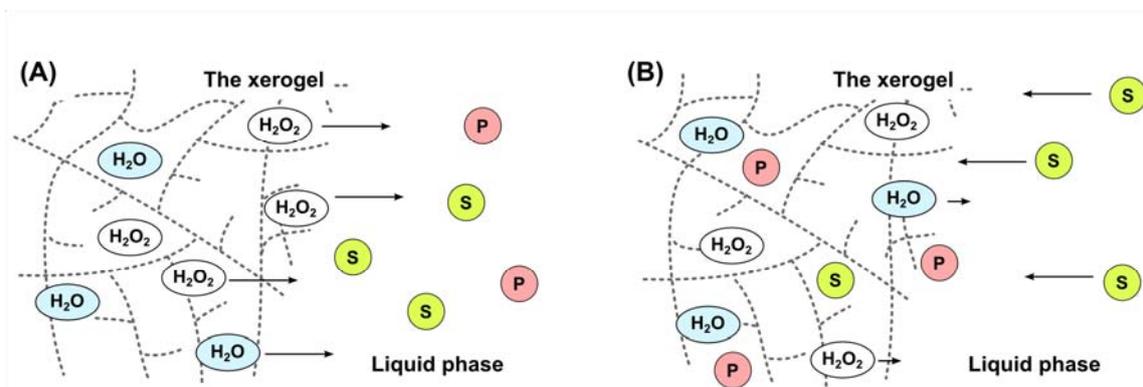
Tentative mechanisms of oxidation with H_2O_2 encapsulated in silica xerogel could be proposed. However, further investigations are needed to prove which of supposed mechanisms (below) taking place.

(1) H_2O_2 and H_2O are fast released from the xerogel to a reaction mixture (Figure 3A). The silica xerogel acts as inert ‘vessel’ for H_2O_2 and H_2O molecules and does not take a part in an oxidation reaction.

(2) Small amounts of H_2O_2 are slowly released from the xerogel to a reaction mixture due to poor solubility of H_2O_2 and H_2O in the solution (Figure 3B). From that reason, the reaction is carried out inside pores of the silica xerogel or on its surface thus additional interactions between the solid support and reagents might occur.

(3) A combination of the two above mechanisms. H_2O_2 and H_2O is released from the composite to a reaction mixture and the silica xerogel acts both as a solid support for the oxidant and also takes a part in an oxidation reaction, because of a specific interactions silica matrix–reagents.

Figure 3. Proposed mechanisms for the xerogel mediated oxidation: $\text{S} \rightarrow \text{P}$. S: substrate, P: oxidation product. (A) H_2O_2 and H_2O are fast released from the xerogel to a reaction mixture. (B) Small amounts of H_2O_2 are slowly released from the xerogel to a reaction mixture.



It seems that the composites may be modified to enhance their properties. It is well-known that silica xerogel doped with metals could be prepared by drying a mixture of aqueous H_2O_2 and silicic acid or silica sol (obtained by e.g., cation exchange method or by hydrolysis of tetraethoxysilane) with a metal

salt or a metal sol (e.g., Mg, Al, Ti, Zr, Sn) [26,27]. If the supposed mechanism 2 or 3 is valid, the metallosilica xerogels could be considered as a matrix for H₂O₂ encapsulation with potential catalytic sites active in oxidation reactions. Moreover, silica xerogels might be modified by addition of water-soluble polymers forming adducts with H₂O₂ such as poly(*N*-vinylpyrrolidone) [28–30] or poly(*N*-vinylcaprolactam) [31,32] to develop tailor-made composites, e.g., with tuned H₂O₂ release rate, which is especially important if the hypothetical oxidation mechanism 1 is correct.

3. Experimental Section

3.1. Equipment

The yield of the reactions was determined by a gas chromatograph coupled with flame ionization detector-GC-FID 6850, Agilent (Santa Clara, CA, USA). Microwave assisted reactions were carried out in a multimode microwave reactor Magnum, Ertec (Wrocław, Poland). FT-IR spectra were obtained by a Biorad STS 165 spectrometer using the KBr pellet technique. FT-Raman spectra were collected by means of an EZRaman-M spectrometer in a range from 250–2340 cm⁻¹, using 785 nm excitation diode laser.

3.2. Materials

Amberlite IR-120 (H⁺ form), octanal, octanoic acid, 2-octanol, 2-octanone, *cis*-cyclooctene, cyclooctene oxide, 1,1,1-trifluoroethanol (TFE), Na₂WO₄·H₂O, UHP, tetrabutylammonium hydrogen sulfate (TBAHS) and 1,6-dibromohexane were purchased from Sigma-Aldrich and used as received. 30% solution of H₂O₂ was from POCH (Gliwice, Poland) and “glass water” R-145 was obtained from Cazet (Łazy, Poland).

3.3. Preparation of Silica Xerogel-Hydrogen Peroxide Composites by the Sol-Gel Method

The composites were prepared according to the literature procedure with some modifications [7]. Silicic acid was obtained from water glass by the cation-exchange method. Water glass (4 g) was diluted with distilled water (16 g). The solution was passed through a bed of cation-exchange resin (Amberlite, 80 g) in a glass column (O.D. 25 mm × 600 mm). The bed was washed with distilled water (40 mL) and effluents were combined and mixed with 30% of H₂O₂ (20 mL) without addition of any H₂O₂ decomposition inhibitor. The sol was poured onto a Petri dish and dried under hood at room temperature for 48h to give 5–10g of the composite (xerogel). Then the hydrogen peroxide content (%H₂O₂) in the composite was determined by iodometric titration and silica content (%SiO₂) was estimated by drying of the xerogel at 150 °C to a constant weight. Water content was approximated as: %H₂O = 100-%H₂O₂-%SiO₂, while loading efficiency (LE) was calculated from the equation: $LE(\%) = (m_x/m_s) \times 100$ where m_x and m_s are weight of H₂O₂ in sol and xerogel, respectively [7].

3.4. Model Reactions

3.4.1. Octanal Oxidation

Octanal (1.05 g, 10 mmol), TBAHS (0.02 g, 0.06 mmol), 1,6-dibromohexane as an internal standard (100 μ L) and the oxidant–equivalent of 12 mmol H_2O_2 (30% H_2O_2 1.36 g; UHP 1.13 g; or the xerogel 1.02 g) were mixed in a vial and heated at 90 °C for 2 h. After that, the reaction mixture was diluted by ethyl acetate (3 mL), dried over MgSO_4 and the solution was and passed through a short pad of MnO_2 to decompose residue of H_2O_2 . The solution was analyzed by GC-FID to determining octanoic acid yield. Retention times of the substrate and the product were compared with authentic samples.

3.4.2. 2-Octanol Oxidation

2-Octanol (0.98 g, 7.5 mmol), $\text{Na}_2\text{WO}_4\cdot\text{H}_2\text{O}$ (0.1 g, 0.3 mmol), TBAHS (0.1 g, 0.3 mmol), 1,6-dibromohexane as an internal standard (100 μ L) and the oxidant–equivalent of 12 mmol H_2O_2 (30% H_2O_2 1.36 g; UHP 1.13 g; or the xerogel 1.02 g) were mixed in a vial and heated at 80 °C for 30 min. After that, the reaction mixture was diluted with ethyl acetate (3 mL), dried over MgSO_4 , and passed through a short pad of MnO_2 to decompose the residue of H_2O_2 . The solution was analyzed by GC-FID to determining 2-octanone yield. Retention times of the substrate and the product were compared with authentic samples.

3.4.3. Cyclooctene Epoxidation

cis-Cyclooctene (0.45 g, 4 mmol), TFE (3.3 mL), $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ (0.013 g, 0.04 mmol), 1,6-dibromohexane and as internal standard (100 μ L) and the oxidant–equivalent of 7 mmol H_2O_2 (30% H_2O_2 0.80 g; UHP 0.65 g; or the xerogel 0.60 g) were mixed in a vial and heated at 60 °C for 3h. After that, the reaction mixture was diluted with dichloromethane (2 mL), dried over MgSO_4 and passed through a short pad of MnO_2 to decompose the residue of H_2O_2 . The solution was analyzed by GC-FID to determining cyclooctene oxide yield. Retention times of the substrate and the product were compared with authentic samples.

3.5. Microwave Assisted Reactions

Microwave assisted reactions were carried out in the microwave reactor equipped with a magnetic stirrer and upright condenser. Temperature was monitored by a universal fiber-optic sensor (FTI-10, FISO, Canada) immersed directly in a reaction mixture. Reactions time and temperature are indicated in Tables 1–3.

4. Conclusions

In summary, the results presented in this paper clearly show that silica xerogel–hydrogen peroxide composites obtained by the sol-gel technique are useful oxidizing agents, with an activity similar to 30% H_2O_2 . Moreover, they have several advantages: they are easy to handle, cheap solids, made from readily available reagents (water glass and 30% H_2O_2). Additionally, unlike other solidified H_2O_2 forms such as sodium percarbonate or sodium perborate, the composite does not change the pH of a

reaction mixture. Silica xerogel–hydrogen peroxide composite exhibits also advantages over UHP. For instance silica (easy to remove by filtration) and H₂O are the only by-products of the silica based material decomposition. Undesired contamination by urea, its decomposition products or other urea side-reactions can be avoided if the silica xerogel is used. In opposition of UHP complex, H₂O₂ is not strongly bonded in the silica matrix thus can be easier released to the reaction solution without heating. Additionally, the xerogel is more easily heated by microwave irradiation than UHP and could be used both as oxidizing agent and as a solid support for microwave assisted solvent free reactions.

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Sample Availability: Samples of the compounds xerogels are available from the authors.

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