Triflic Acid-Functionalized Silica-Coated Magnetic Nanoparticles as a Magnetically Separable Catalyst for Synthesis of *gem*-Dihydroperoxides

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Abstract: Triflic acid-functionalized silica-coated magnetic nanoparticles $[\gamma-Fe_2O_3@SiO_2-TfOH]$ were readily prepared and identified as an effictive catalyst for the transformation of aldehydes or ketones into their corresponding *gem*-dihydroperoxides with 30% aqueous hydrogen peroxide. The catalyst was easily separated by magnetic decantation and the re-

Introduction

With increasing environmental concerns, the development of efficient and recoverable heterogeneous catalysts has become an important research field. In this context, nanoparticles as heterogeneous catalysts have attracted a great deal attention due to their interesting structures and high catalytic activities.^[1] Furthermore, nanometer-sized particles are easily dispersible in solution by forming stable suspensions.^[2] In spite of these advantages, the tedious recycle of such small particles via expensive ultra-centrifugation has limited their application. To further address the issues of recyclability and reusability, magnetic nanoparticles (MNPs) have emerged as excellent supports amenable to simple magnetic separation.^[3] Moreover, magnetic nanoparticles can be functionalized easily through appropriate surface modifications, which are able to load various functionalities.^[4-6]

Organic *gem*-dihydroperoxides (DHPs) have been shown to possess intriguing biological and pharmaceutical properties such as antiparasitic and antimicrobial activity.^[7] They are also used as allergens, antifungal and antitumour agents, as well as inhibitors of enzymes.^[8] In addition, these compounds are synthetic intermediates for the preparation of various cyclic peroxides such as 1,2,4,5-tetraoxacycloalkanes,^[9] 1,2,4trioxane,^[10] 1,2,4,5,7,8-hexaoxonane,^[11] macrocyclic covered catalyst was reused for seven cycles without significant loss of catalytic activity.

Keywords: aldehydes; *gem*-dihydroperoxides; functionalized silica-coated magnetic nanoparticles; ketones; magnetic catalysts

endoperoxides,^[12] and acylic analogues with a variety of functional groups.^[13] These cyclic peroxides have been found to exhibit significant antimalarial activities.^[14] *gem*-Dihydroperoxides have also been utilized as oxidants for epoxidation,^[15,16] sulfoxidation,^[17] and synthesis of oligodeoxyribonucleotides,^[18] and as initiators for radical polymerization.^[19] Generally, ozonolysis of ketone enol ethers or α -olefins in the presence of H₂O₂ had been widely used for the synthesis of gem-DHPs.^[9a] The preparation of gem-DHPs has also been accomplished through the reaction of acetals and enol ethers with H_2O_2 in the presence of tungstic acid,^[20] or BF₃·OEt₂,^[21] or hydroperoxide re-arrangement of bicyclic hydroperoxides.^[22] In spite of their potential utility, these methods involved the need for the prior synthesis of the suitable starting substrates.^[20-22] In addition, the selectivity of ozonolysis is poor and the process cannot be used for substrates containing ozone-sensitive functional groups.^[9a] In this respect, directly employing ketones and aldehydes under oxidative conditions turned out to be the most facile and effective method to synthesize gem-DHPs. Some catalysts such as stannous chloride,^[23] strontium chloride,^[24] ceric ammonium nitrate,^[25] phosphomolybdic acid,^[26] camphorsulfonic acid,^[27] H_2SO_4 ,^[28] NaHSO₄·SiO₂,^[29] iodine,^[30] or Re₂O₇^[31] have been employed to accomplish this reaction. However, some of the reported methods involved the use of



Scheme 1. Synthesis of *gem*-DHPs with 30% H_2O_2 in the presence of γ -Fe₂O₃@SiO₂-TfOH.

Lewis acids or Brønsted acids. These traditional acids are corrosive and produce significant amounts of waste, which limits their usefulness and causes serious environmental concerns. Furthermore, long reaction times,^[27,30] unsatisfactory yields,^[28] the use of highly concentrated $H_2O_2^{[26,27]}$ or relatively expensive reagents.^[31] are other disadvantages of some of these methods. Besides, in these methods, catalysts are destroyed during the work-up and cannot be recovered.^[23-28] The catalyst-free synthesis of gem-DHPs from ketones and aldehydes with hydrogen peroxide in dimethoxyethane^[32] or with molecular oxygen under light irradiation^[33] proceeded under mild conditions, but required long reaction times and gave low yields of products. Due to their importance and useful properties, the development of an efficient, general and environmentally benign method for the preparation of these widely used gem-DHPs is a major challenge in synthetic organic chemistry.

Recently, we have discovered that magnetic Fe_3O_4 nanoparticles are excellent catalysts for the synthesis of quinoxalines^[34] and 2,3-dihydroquinazolin-4(1H)ones.^[35] We have developed an efficient method for one-pot reductive amination of carbonyl compounds using NaBH₄ in the presence of the magnetically recoverable y-Fe₂O₃@HAP-SO₃H.^[36] Immobilization of $HClO_4^{[37]}$ or $H_3PW_{12}O_{40}^{[38]}$ onto the silica-coated magnetic nanoparticles has also been successfully achieved. As a continuation of our interest in developing efficient and environmental benign synthetic methodologies,^[39] we report herein on the preparation of a new type of magnetically separable y-Fe₂O₃@SiO₂-TfOH nanoparticles and their application for the synthesis of gem-DHPs at room temperature (Scheme 1).

Results and Discussion

Although silica-supported triflic acid (TfOH-SiO₂) was introduced by Liu and co-workers,^[40] the tedious recycling of the catalyst by filtration and inevitable

loss of solid catalyst in the separation are some of the drawbacks. Therefore, we decided to design a novel version of silica-supported TfOH to facilitate a more efficient recycling of this catalyst. For this purpose, we prepared the triflic acid-functionalized silica-coated magnetic nanoparticles [γ -Fe₂O₃@SiO₂-TfOH] and, after characterization, the peroxidation of carbonyl compounds was selected to investigate its catalytic activity and recyclability.

To prepare γ -Fe₂O₃@SiO₂-TfOH, we have first chosen a known nanomagnet γ -Fe₂O₃, which can be easily prepared by coprecipitation of ferrous (Fe^{2+}) and ferric (Fe³⁺) ions in a basic aqueous solution followed by thermal treatment according to the reported procedure.^[37] Coating of a layer of silica on the surface of γ -Fe₂O₃ nanoparticles was achieved by sonication of a γ -Fe₂O₃ suspension in an alkaline ethanolwater solution of tetraethyl orthosilicate (TEOS). Then, triflic acid was added to a suspension of y- $Fe_2O_3@SiO_2$ in Et₂O, while dispersed by sonication. The mixture was concentrated and the residue was heated at 70°C for 24 h under vacuum to obtained triflic acid-functionalized silica-coated magnetic nanoparticles [y-Fe₂O₃@SiO₂-TfOH] (Scheme 2). The loading of triflic acid moiety on surface was determined by means of back tritration and pH analysis $(0.30 \text{ mmol g}^{-1}, 10 \text{ mg} = 0.003 \text{ mmol of } CF_3SO_3H).$

The FT-IR spectra of y-Fe₂O₃@SiO₂-TfOH displayed strong bands around 3440, 1078, and 639 cm^{-1} , which are ascribed to the characteristic bands of ν (O–H), ν (Si–O), and ν (Fe–O) in magnetic nanoparticles. This demonstrated the successful in loading of TfOH onto the magnetic nanoparticles, whereby a relatively weak absorption band around 1170 cm⁻¹ for v (S=O) was derived from TfOH (Figure 1). The energy dispersive spectrum (EDS) showed that the mass percentages of Fe, Si, O, C and S are 1.89%, 38.62%, 55.31%, 3.85% and 0.33%, respectively (Figure 2). XRD measurements of γ -Fe₂O₃@SiO₂ and y-Fe₂O₃@SiO₂-TfOH exhibit diffraction peaks at around 35.5°, 43.1°, 62.8°, 54° corresponding to the (311), (400), (511) and (440) faces (Figure 3). The observed diffraction peaks agree well with the tetragonal structure of maghemite.^[33] It is clear that no other phases except the maghemite are detectable. The average crystallite size of γ -Fe₂O₃@SiO₂-TfOH particles was calculated to be ~50 nm by Scherrer's equation for the (311) reflection, which is in good accordance with transmission electron microscopy (TEM) results (Figure 4). The specific surface area of



Scheme 2. Synthesis of γ -Fe₂O₃@SiO₂-TfOH.

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Figure 1. IR spectra of γ -Fe₂O₃@SiO₂-TfOH.



Figure 2. EDS spectrum of γ -Fe₂O₃@SiO₂-TfOH.



Figure 3. XRD pattern of γ -Fe₂O₃@SiO₂ and γ -Fe₂O₃@SiO₂-TfOH.

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Figure 4. TEM image of γ-Fe₂O₃@SiO₂-TfOH.

Table 1. Influence of different catalysts on the reaction of cyclohexanone with 30% aqueous H_2O_2 .^[a]

$OOH = 0 \frac{30\% \text{ H}_2\text{O}_2 \text{ (4 equiv.), catalyst}}{\text{MeCN, r.t.}} OOH \\ OOH$				
Entry	Catalyst (10 mol%)	Time [min]	Yield [%] ^[b]	
1	nano ZnO	240	0	
2	nano TiO ₂	240	0	
3	nano CuO	240	0	
4	nano Al(OH) ₃	240	0	
5	nano ZnFe ₂ O ₄	240	0	
6	nano Fe ₃ O ₄	240	0	
7	nano γ -Fe ₂ O ₃	240	0	
8	γ-Fe ₂ O ₃ @HAP-SO ₃ H	240	18	
9	SiO_2 (50 mg)	240	0	
10	TfOH	120	80	
11	SiO ₂ -TfOH	120	86	
12	γ-Fe ₂ O ₃ @SiO ₂ -TfOH	80	96	

[a] Experimental conditions: cyclohexanone (1 mmol), 30%
 H₂O₂ (4 mmol), and catalyst (0.10 mmol) in 5 mL of CH₃CN at room temperature.

^[b] Isolated yields.

the powders was determined by use of the Brunauer– Emmett–Teller (BET) method. BET results showed that the average surface area was $50 \text{ m}^2 \text{g}^{-1}$.

In initial attempts, the activity of the prepared catalyst as described above was measured in the model reaction between cyclohexanone and 30% aqueous H_2O_2 in acetonitrile. From Table 1, it was clear that γ -Fe₂O₃@SiO₂-TfOH worked remarkably well to give the desired product within 80 min in 96% yield. For comparison, the model reaction was carried out using liquid TfOH as the homogeneous catalyst, and only 80% yield was obtained (Table 1, entry 10). This result suggested that γ -Fe₂O₃@SiO₂-TfOH was a more effective catalyst than the original homogeneous one. Besides, this novel catalyst was superior to triflic acid

Table 2. Optimization of the reaction conditions.^[a]

\langle	>=0 <u>30% H₂C</u>	⁰ ₂ -[γ-Fe ₂ O ₃ solvent. r	@SiO ₂ -TfOH]	\cdot	.00H 00H
		,			0011
Entry	Catalyst load- ing [mol%]	Solvent	$\begin{array}{l} 30\% \ H_2O_2 \\ (equiv.) \end{array}$	Time [min]	Yield [%] ^[b]
1	no	MeCN	4	180	0
2	10	CH_2Cl_2	4	120	81
3	10	EtOAc	4	120	77
4	10	Et_2O	4	120	50
5	10	MeCN	4	80	96
6	5	MeCN	4	120	84
7	15	MeCN	4	120	96
8	20	MeCN	4	120	95
9	10	MeCN	2	180	66
10	10	MeCN	3	120	90
11	10	MeCN	5	120	96
12	10	MeCN	6	120	92

^[a] *Experimental conditions*: cyclohexanone (1 mmol) in 5 mL of solvent at room temperature.

^[b] Isolated yields.

absorbed on silica gel (TfOH-SiO₂)^[40] with respect to yield of the product under identical conditions (Table 1, entry 11). The reason for the improved catalytic activity may due to higher surface areas of nanoheterogeneous catalysts.^[41] Although scale γ-Fe₂O₃@HAP-SO₃H is well known to be a good catalyst for some organic reactions,^[36,42] its catalytic activity for this reaction was lower than γ -Fe₂O₃@SiO₂-TfOH (Table 1, entry 8). Various other nano materials such as ZnO, TiO₂, CuO, Al(OH)₃, ZnFe₂O₄, Fe₃O₄ and γ -Fe₂O₃ were also tested for this transformation, however, no expected product formation was observed.

For further studies regarding the effect of various solvents, the above reaction was conducted in the presence of γ -Fe₂O₃@SiO₂-TfOH with various solvents such as acetonitrile, dichloromethane, ethyl acetate, and diethyl ether. The results indicated that different solvents affected the efficiency of the reaction (Table 2). The best conversion was observed when the reaction was performed in acetonitrile in which probably solvent polarity plays an important role.[24,31] Moreover, we found that the yields were obviously affected by the amount of catalyst. It was found that 10 mol% of γ -Fe₂O₃@SiO₂-TfOH was sufficient to catalyze the reaction and the use of higher amounts of catalyst did not increase the yields significantly. On the other hand, when the reaction was attempted without the addition of catalyst, no desired product was obtained (Table 2, entry 1). 4 equivalents of H_2O_2 were necessary to produce the product in satisfying yield, and lower yields of the product were observed when using only 2 or 3 equivalents of H_2O_2 (Table 2, entries 9 and 10).

Having these results in hand, we then investigated the scope and limitations of the method. As shown in Table 3, many acyclic aliphatic ketones (Table 3, entries 1-9) were effectively transformed into their corresponding gem-dihydroperoxides in 86-96% yields within 80-120 min at room temperature. Steric effects in the α -position of the carbonyl group play a key role in facilitating the reaction because of the fact that replacing a hydrogen atom with a methyl group, for example, pentan-3-one (1g), results in a decrease of the reaction yield (88%, Table 3, entry 7). Similarly, various cyclic ketones such as cyclopentanone, cyclohexanone and its derivatives, cycloheptanone, cyclododecanone, and 1H-inden-2(3H)-one (Table 3, entries 10-21) furnished the products in high to excellent yields. 2-Adamantanone (entry 22) and 2-norbornanone (entry 23), having high steric hindrance, were still reactive and the corresponding gem-dihydroperoxides were obtained in 95% and 94% yields, respectively. Furthermore, no products of ring expansion were observed.^[43] When aromatic ketones were used, the yields were somewhat lower (entries 24 and 25). In addition, seven aliphatic aldehydes were suitable substrates to produce gem-dihydroperoxides in high yield, as shown in entries 26-28. The reaction of aromatic aldehydes having electron-donating groups also proceeded efficiently (Table 3, entries 29-32), while with a compound having an electron-withdrawing 4-nitrobenzaldehyde group, such as (Table 3, entry 33), no corresponding gem-dihydroperoxide was isolated.

The reusability is one of the important properties of this catalyst. In this work, we examined the possibility of recovery and reuse of γ -Fe₂O₃@SiO₂-TfOH. After completion of the model reaction, the catalyst was recovered from the reaction mixture simply by applying an external magnet. Then the recovered catalyst was washed with diethyl ether, and dried at room temperature. The recovered catalyst could be added to fresh substrates under identical conditions for seven runs without a noticeable drop in the product yield and its catalytic activity. (Figure 5). The slight decrease of catalytic activity should be due to the normal loss of the catalyst during the work-up stage. No quantifiable amount of leached Fe was detected in the filtrates as determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). To determine of the leaching of the acid, the model reaction was carried out in the presence of γ -Fe₂O₃@SiO₂-TfOH for 30 min and at that point the catalyst was removed by external magnet. The residual solution was then allowed to react, but no significant progress was observed after 1 h. Therefore, these experiments are a further testimony to the heterogeneous nature of the catalytic system. Furthermore, the TEM images of the used catalyst did not show any significant change in the shape and size of catalyst

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Table 3. Synthesis of gem-dihydroperoxides in the presence of γ -Fe₂O₃@SiO₂-TfOH.

Entry	Substrate	Product	Time [min]	Yield [%] ^[a]	Ref.
1	O U U 3	2a	80	92	[29]
2		2b	80	96	[29]
3	O U U 6	2c	80	94	[30b]
4	O (H) ₇	2d	80	93	[29]
5	O U U B	2e	80	92	[24]
6	O U U G	2f	100	89	[30a]
7	o J	2g	100	88	[33]
8		2h	100	87	[30a]
9	° – – – – – – – – – – – – – – – – – – –	2j	90	86	[23]
10	○ ► ⁰	2k	120	95	[33a]
11	O	2k	80	96	[33a]
12	C C	21	100	93	[33a]
13	₩ C	2m	90	95	[33a]
14	–∕o	2n	80	96	[33a]
15	o	20	80	95	
16	→-{>=0	2p	80	96	[32]
17		2q	80	90	
18		2r	80	81	
19	\bigcirc	2s	80	91	[32]
20		2t	80	93	[32]
21		2u	80	84	
22	₽,°	2v	80	95	[32]
23	0	2w	80	94	

Table	Table 3. (Continued)						
Entry	Substrate	Product	Time [min]	Yield [%] ^[a]	Ref.		
24	O O	2x	480	41	[24]		
25	MeO	2y	480	42	[24]		
26	H H	2z	480	76	[27]		
27	H H	2 aa	480	78			
28	H H	2ab	480	75	[32]		
29	Н	2ac	480	66	[29]		
30	MeO	2ad	480	69	[32]		
31	Н	2ae	480	62	[24]		
32	CI H	2af	480	78	[24]		
33	O ₂ N H	2ag	480	0			

^[a] Isolated yield.



Figure 5. Reusability of the catalyst using cyclohexanone as substrate.

particles even after seven times reaction cycles, which proved its robustness (see Supporting Information, Figure S1).

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Conclusions

In conclusion, we have immobilized, for the first time, triflic acid onto magnetic γ -Fe₂O₃@SiO₂ and applied the immobilized catalyst (γ -Fe₂O₃@SiO₂-TfOH) in the dihydroperoxidation of a wide variety of carbonyl compounds. The corresponding *gem*-dihydroperoxides were obtained in moderate to high yields with aqueous H₂O₂ (30%) as oxidant. Product separation and catalyst recycling are easy and simple with the assistance of an external magnet. The catalyst can be recovered and reused for seven times with little loss of activity.

Experimental Section

Synthesis of Triflic Acid-Functionalized Silica-Coated Magnetic Nanoparticles

To a suspension of γ -Fe₂O₃@SiO₂ (1 g) in Et₂O (50 mL), TfOH (0.30 mmol) was added. The mixture was irradiated in the ultrasonic bath for 60 min at room temperature. The Et₂O was removed and the residue was heated at 70°C under reduced pressure for 24 h to afford γ -Fe₂O₃@SiO₂-TfOH (0.30 mmol g⁻¹, 10 mg=0.0030 mmol of TfOH).

General Procedure for Synthesis of *gem*-Dihydroperoxides

A mixture of carbonyl compound (1 mmol), 30% aqueous H_2O_2 (4.0 mmol) and γ -Fe₂O₃@SiO₂-TfOH (0.1 mmol) in MeCN (5 mL) was stirred at room temperature. The progress of reaction was monitored by TLC using *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine dihydrochloride as a chromatogenic reagent. After completion of the reaction, the catalyst was separated with the aid of an external magnet. The mixture was diluted with water (5 mL), extracted with ethyl acetate. The combined organic layer was washed with brine, dried (MgSO₄) and the solvent was evaporated under vacuum. The residue was purified by short column chromatography on silica gel using ethyl acetate/petroleum ether as solvent to provide the pure products.

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