

Alkanedisulfamic acid functionalized silica-coated magnetic nanoparticles as a reusable efficient nanocatalyst for synthesis of *gem*-dihydroperoxides and 1,2,4,5-tetraoxanes

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ABSTRACT

Alkanedisulfamic acid functionalized silica-coated magnetic nanoparticles (ADSA-MNPs) were used as effective, low-cost and reusable solid heterogeneous nanomagnetic catalysts for conversion of aldehydes and ketones to corresponding *gem*-dihydroperoxides and 1,2,4,5-tetraoxanes using aqueous hydrogen peroxide (30% w/w in H₂O) at room temperature. These compounds are important key intermediates in preparation of anti-malaria drugs. The reactions proceeded in high rates and excellent yields. Since the catalyst was separated facilely from the reaction mixture by an external magnet and was reused six times without considerable loss of catalytic activity, this methodology is environmentally friendly. It is notable that it is the first report on using a nanocatalyst in the synthesis of *gem*-dihydroperoxides and 1,2,4,5-tetraoxanes from aldehydes and ketones up to now.

Keywords: *Gem*-dihydroperoxide; 1,2,4,5-tetraoxanes; Alkanedisulfamic acid functionalized silica-coated magnetic nanoparticles; Aldehydes; Ketones; Hydrogen peroxide.

1. Introduction

Gem-dihydroperoxides (GDHPs) as the rather stable peroxidic derivatives of ketones and aldehydes, have been a matter of interest due to their relevance to peroxidic antimalarial drugs [1-3]. Besides, *gem*-dihydroperoxides are the important fundamental intermediates in the synthesis of some categories of peroxides including tetraoxanes [4-6], silatetraoxanes [7], spirobisperoxyketals [8,9], bisperoxyketals [10], and 1,2,4,5-tetraoxacycloalkanes [11,12]. Also, *gem*-dihydroperoxides have been used as initiators in radical polymerization processes because of the peroxidic bond in their structures [13]. Additionally, they can be employed as suitable solid oxidants in many oxidative reactions such as oxidation of alcohols [14] and sulfides [15,16], epoxidation of α,β -unsaturated ketones [17,18], enantioselective oxidation of 2-substituted-1,4-naphthoquinones [19] and several other organic reactions [20,21]. Generally, two methods have been reported for the synthesis of *gem*-dihydroperoxides:

(I) reaction of ketals with H₂O₂ in the presence of tungstic acid [22], or BF₃.Et₂O [23], (II) ozonolysis of ketone enol ethers or α -olefines by using aqueous H₂O₂ [11, 24]. Nevertheless, these major methods endure some disadvantages such as concentrated H₂O₂ and an extra acid requirement, limited substrate range and production of various peroxidic products, low yield and rough reaction conditions [25]. In addition, poor selectivity and restriction caused by the existence of ozone sensitive functional groups in substrates are additional limitations in the ozonolysis reaction. Consequently, to eliminate these drawbacks, peroxidation of aldehydes and ketones by aqueous H₂O₂ has been reported in the presence of molecular iodine as the catalyst recently [26,27]. Several Lewis or Bronsted acids, such as ceric ammonium nitrate (CAN) [28], camphor sulfuric acid (CSA) [29], NaHSO₄.SiO₂ [30], Re₂O₇ [31], PMA [32] and bismuth (III) triflate [33] have been explored lately as the catalysts for preparation of *gem*-dihydroperoxides. Besides, magnetic nanocatalysts have been in the center of attention recently because of their reusability and higher efficiency [34]. Due to the value of *gem*-dihydroperoxides and 1,2,4,5-tetraoxanes as the

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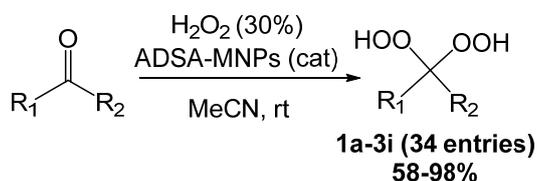
precursors for the synthesis of anti-malaria drugs, in continuation of our interest to modify this method and use novel and improved catalysts, [25, 35], herein, we like to demonstrate the alkanedisulfamic acid functionalized silica-coated magnetic nanoparticles as an inexpensive and efficient recoverable solid nanocatalyst in the synthesis of *gem*-dihydroperoxides from aldehydes and ketones with aqueous H₂O₂ (30% w/w in H₂O) at room temperature (Scheme 1). Equally important, this nanocatalyst was successfully used for facile synthesis of 1,2,4,5-tetraoxanes by direct condensation of obtained *gem*-dihydroperoxides from different ketones (Scheme 2). Alkanedisulfamic acid functionalized silica-coated magnetic nanoparticles has been applied as a catalyst in the synthesis of Mono-, Bis- and Tris [bis (4-hydroxycoumarinyl) methanes] [36].

It is noteworthy to mention that there have not been any reports on using a nanocatalyst in the synthesis of *gem*-dihydroperoxides and 1,2,4,5-tetraoxanes from aldehydes and ketones up to now.

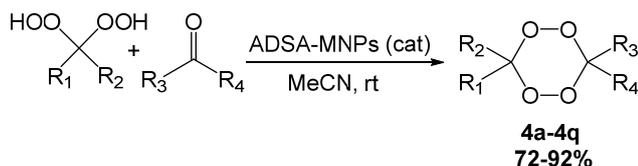
2. Experimental

Solvents, reagents, and chemical materials were obtained from Aldrich and Merck chemical companies and purified prior to use. Nuclear magnetic resonance spectra were recorded on JEOL FX 90Q and Bruker 300 MHz using tetramethylsilane (TMS) as an internal standard. Infrared spectra were recorded on a PerkinElmer GX FT IR spectrometer (KBr pellets).

Caution: Although we did not encounter any problem with *gem*-dihydroperoxides, peroxides are potentially explosive and should be handled with precautions; all reactions should be carried out behind a safety shield inside a fume hood and heating should be avoided.



Scheme 1. Conversion of aldehydes and ketones to corresponding *gem*-dihydroperoxides catalyzed by ADSA-MNPs.



Scheme 2. Synthesis of 1,2,4,5-tetraoxanes catalyzed by ADSA-MNPs

2.1. General procedure for preparation of (ADSA-MNPs)

This magnetic nanocatalyst has been prepared and characterized as the reported procedure before [36].

2.2. General procedure for synthesis of *gem*-dihydroperoxides

To a mixture of carbonyl compound (1 mmol) and ADSA-MNPs (0.01 g) in MeCN (3mL), aqueous H₂O₂ (30% w/w in H₂O, 1 mL, 9.8 mmol) was added and the mixture was stirred at room temperature for an appropriate time (Tables 2-5). After the completion of the reaction as monitored by thin-layer chromatography (TLC), the nanocatalyst was separated with a magnet and the organic layer was evaporated under reduced pressure to afford pure *gem*-dihydroperoxides (Tables 2-4). Products were characterized on the basis of their melting points, elemental analysis and IR, ¹H NMR, and ¹³C NMR spectral analysis. The amount of peroxide in products was determined by iodometric titration.

2.3. Catalyst Recovery and Reuse

The reusability potential of the catalyst was examined in the reaction of cyclohexanone with aqueous H₂O₂ (30% w/w in H₂O) at room temperature in the presence of recovered ADSA-MNPs. ADSA-MNPs was easily separated from the mixture of the reaction with a powerful magnet. It was reused after washing with CHCl₃ and drying at 60°C.

2.4. General procedure for synthesis of tetraoxanes

To a mixture of ketone (1 mmol) and ADSA-MNPs (0.01 g) in MeCN (3 mL), *gem*-dihydroperoxide (1 mmol) was added and the mixture was stirred at room temperature for an appropriate time (Tables 5). After the completion of the reaction as monitored by thin-layer chromatography (TLC), the nanocatalyst was separated with a magnet and then the organic layer was evaporated under reduced pressure to afford pure 1,2,4,5-tetraoxanes (Table 5). Products were characterized on the basis of their melting points, elemental analysis and IR, ¹H NMR, and ¹³C NMR spectral analysis (See supplementary data).

3. Results and Discussion

The nanocatalyst was characterized by different techniques such as FT-IR, SEM, TGA and X-ray diffraction analysis (Figures 1-4). The study of FT-IR spectra of (a) MNP, (b) CMNP, (c) AEAP-MNPs and (d) ADSA-MNPs, which is illustrated in Fig. 1

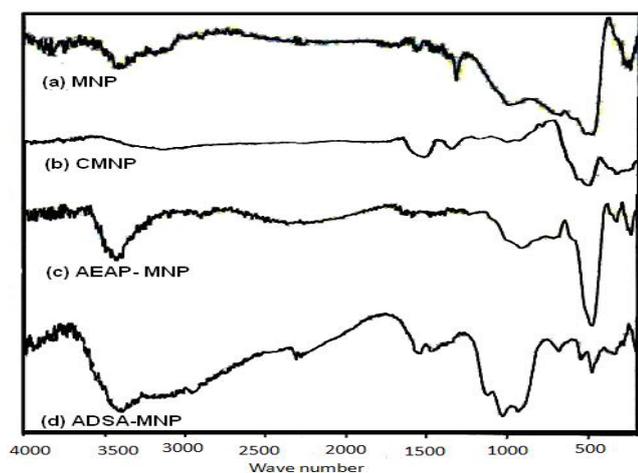


Fig. 1. FT-IR spectra of (a) MNP, (b) CMNP, (c) AEAP-MNPs and (d) ADSA-MNPs.

confirmed the formation of ADSA-MNPs since the significant peaks for N-H, S=O and O-H were observed. The size of the nanoparticles was determined by scanning electron microscopy (SEM). The SEM micrographs (Fig. 2) showed that the ADSA-MNPs were spherical in shape and that their average size was about 38 nm.

The thermal properties of ADSA-MNPs were analyzed by thermal gravimetric analysis at 20–850°C under nitrogen (Fig. 3). The primary weight loss at up to 160°C was related to the removal of physically adsorbed solvent. The rate of weight loss between 160 and 500°C was relatively slow, showing that the ADSA-MNPs have a reasonably high thermal stability at up to 500 °C. The maximum rate of weight loss for these nanoparticles began at 500°C. There was a well-defined mass loss of 50% at between 160 and 700°C, related to the breakdown of the sulfuric acid and alkylamine moieties.

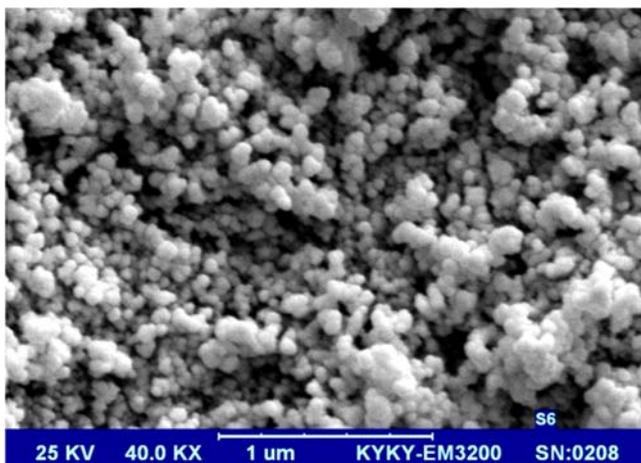


Fig. 2. SEM images of ADSA-MNPs.

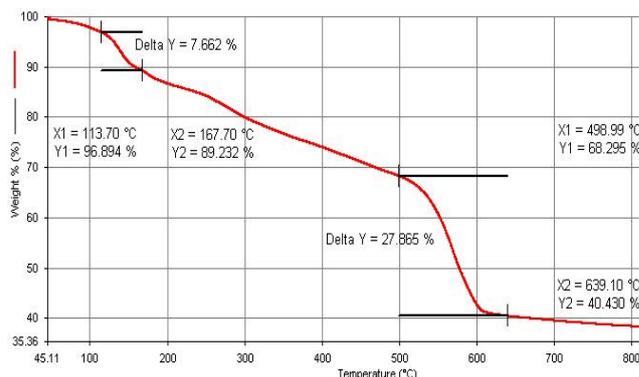


Fig. 3. The thermogram of ADSA-MNPs.

The X-ray diffraction patterns of the ADSA-MNPs showed that the cubic structure of the magnetite was well preserved after introduction of the AEAPS and sulfuric acid functionality [40]. The intensity of the 41.6° reflection of the ADSA-MNPs decreased after introduction of the sulfuric acid group (Fig. 4).

Various reaction parameters were studied to produce 1,1-dihydroperoxycyclohexane through the model reaction of cyclohexanone with aqueous H₂O₂ (30% w/w in H₂O) under the catalytic effect of ADSA-MNPs using different solvents and the results were summarized in Table 1. As shown in this Table, the best result in terms of yield and reaction time was provided by using MeCN as the solvent of choice at room temperature with 0.01 g of catalyst loading (Table 1, entry 8). With optimized reaction conditions in hand (aldehyde or ketones (1 mmol), aqueous H₂O₂ (30% w/w, 1mL), 0.01 g catalyst, MeCN (3 mL, r.t), we began to study the scope of the reaction using a range of aromatic aldehydes and ketones (Table 2), cyclic aliphatic ketones (Table 3) and side chain aliphatic aldehydes and ketones (Table 4).

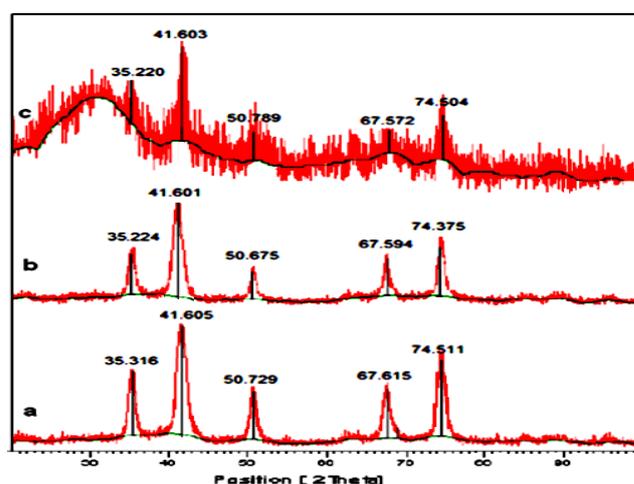
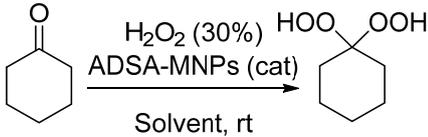


Fig. 4. X-ray diffraction patterns of (a) MNP, (b) AEAP-MNPs and (c) ADSA-MNPs.

Table 1. Screening of reaction parameters for formation of dihydroperoxycyclohexane.


Entry ^a	Solvent	ADSA-MNPs (g)	Time (min)	Yield (%)
1	Et ₂ O	0.01	25	64
2	EtOAc	0.01	14	82
3	CH ₂ Cl ₂	0.01	45	42
4	CHCl ₃	0.01	41	55
5	CCl ₄	0.01	52	40
6	CH ₃ CN	-	300	5
7	CH ₃ CN	0.05	15	75
8	CH ₃ CN	0.08	12	88
9	CH ₃ CN	0.01	7	98
10	CH ₃ CN	0.015	5	91
11	CH ₃ CN	0.02	5	75

^aConditions: 1 mmol cyclohexanone, amount of H₂O₂ in all entries is 1 mL (9.8 mmol).

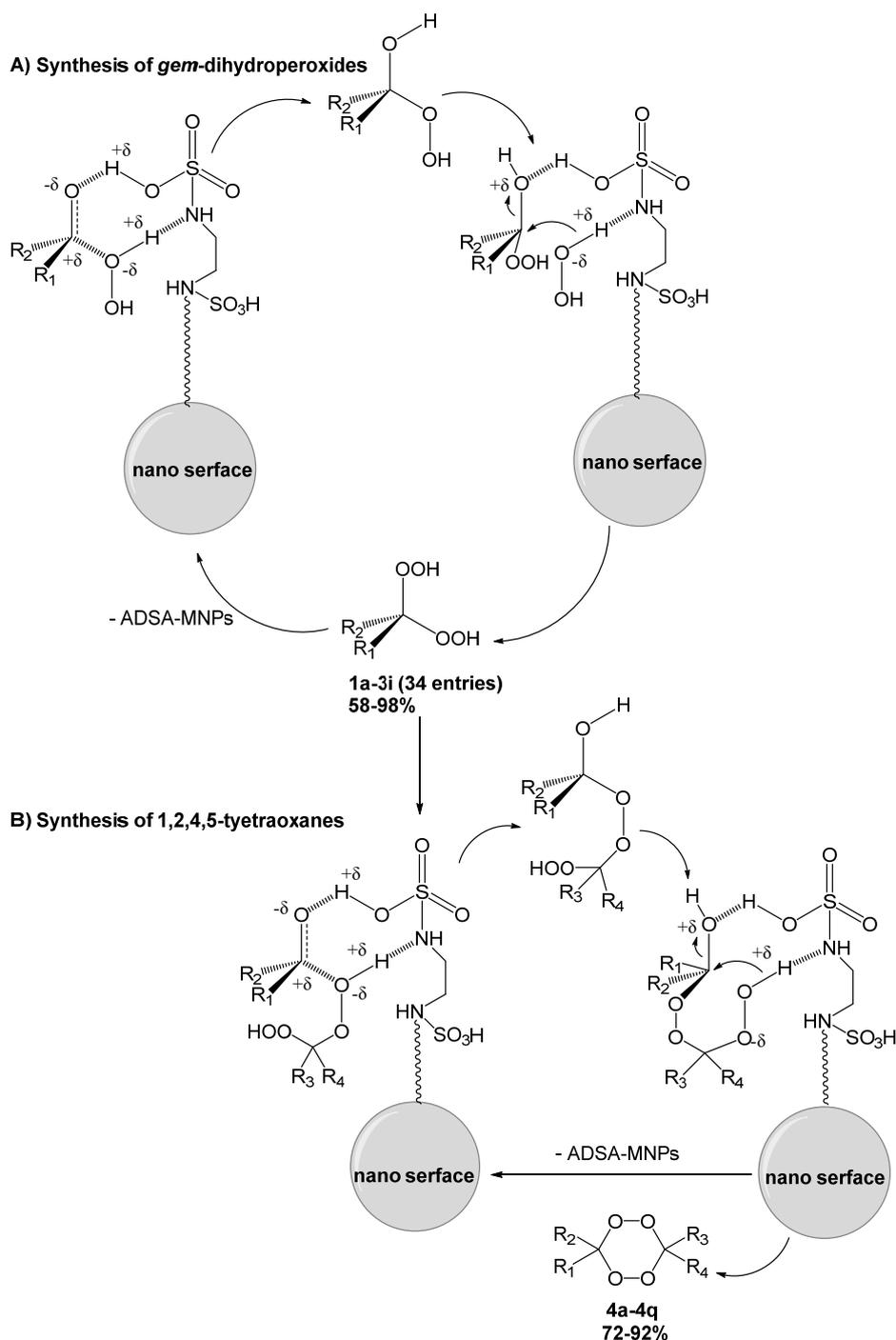
According to the summarized results in Tables 2-4, generally, the aromatic aldehydes and ketones, which were substituted by electron-withdrawing substituents did not react at all or reacted in very long reaction times with nearly low yields as it was also reported by Katja Zmitek and Co-workers had an explanation for this case [28]. They reported that the transition state of carbonyl peroxidation reaction had positive charge on carbonyl group. So, this reaction has high negative Hammett reaction constant ($\rho = -2.76$), which suggests a transition state with a more developed charge in the rate-determining step [28]. For example, we observed that 4-*N,N*-dimethylamino benzaldehyde reacted faster than 4-chlorobenzaldehyde (Table 2, entry 1f). On the other hands, 4-nitro benzaldehyde was converted to *gem*-dihydroperoxide very slowly in very low conversion (15%) and was decomposed after 0.5 hour due to powerful electron-withdrawing effect of NO₂ group (Table 2, entry 1c). Also, interestingly, both cyclic and side chain aliphatic ketones reacted faster than the aromatic ketones to afford the corresponding *gem*-dihydroperoxides comparatively in higher yields. For cyclic ketones, cyclohexanone reacted faster than cyclopentanone in higher yield (Table 3, entries 2a and 2b). Therefore, based on experimental evidence, we suggest that ADSA-MNPs activate both carbonyl group and hydrogen peroxide. ADSA-MNPs have a powerful acidic functional group (SO₃H), so it generates H⁺ that activates the carbonyl group [36]. On

the other hand, the nitrogen atoms of ADSA-MNPs (NH) activate hydrogen peroxide via hydrogen bonding (Scheme 3). In Addition, due to the catalyst's nano size, the surface of the catalyst has highly increased which can help accelerating the reaction.

In addition, it is interesting that carbonyl group of aliphatic aldehydes reacted with only one molecule of hydrogen peroxide and 1,1-hydroxyhydroperoxide derivatives were formed instead of their expected DHPs (Table 4, entries 3a and 3b, Scheme 4).

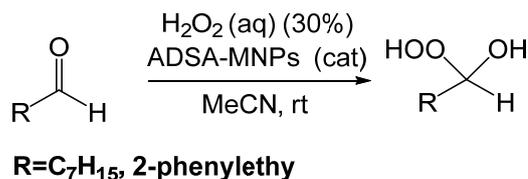
Also, terephthalaldehyde and benzil reacted as the dicarbonyl compounds and both of the carbonyl groups were successfully converted to *gem*-dihydroperoxide after 300 and 700 minutes, respectively (Table 3, entries 1i and 1j). Additionally, we successfully converted nicotinaldehyde, quinoline-2-carbaldehyde and thiophene-2-carbaldehyde as a heterocyclic aldehyde to corresponding *gem*-dihydroperoxide without any by-product production (Table 2, entries 1g, 1h and 1p). Like our other reported work [35a, 38], benzophenone was recovered intact after 200 minutes (Table 2, entry 1q).

In the next step, we used some of the synthesized *gem*-dihydroperoxides as nucleophiles. These *gem*-dihydroperoxides reacted with ketones, so a variety of 1,2,3,4-tetraoxanes was produced. (Scheme 2, Table 5) Reaction conditions were similar to the synthesis of *gem*-dihydroperoxides condition.



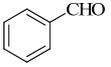
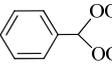
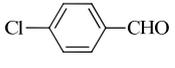
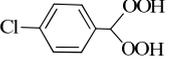
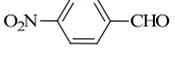
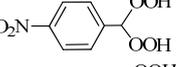
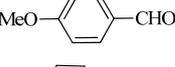
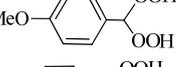
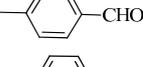
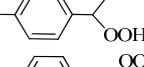
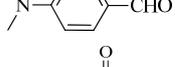
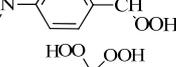
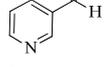
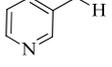
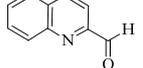
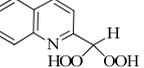
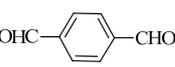
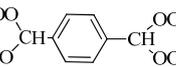
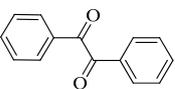
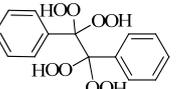
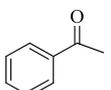
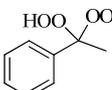
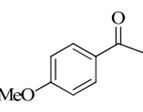
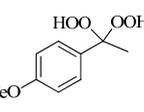
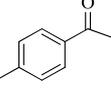
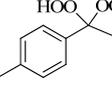
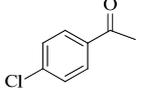
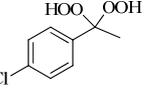
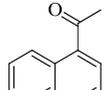
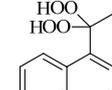
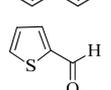
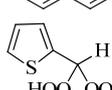
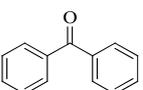
Scheme 3. Suggested mechanism to demonstrate catalytic effect.

Finally, this method for peroxidation of cyclohexanone was compared with other reported methodologies (Table 6). Based on the results, this methodology improved the reaction times, yields and reaction conditions adequately and acceptably. In addition, in comparison with other methodologies less amounts of the catalyst were required to accomplish the reaction.



Scheme 4. Peroxidation of aliphatic aldehydes.

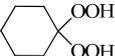
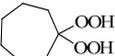
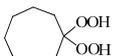
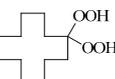
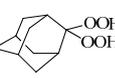
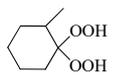
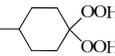
Table 2. Peroxidation of aromatic ketones and aldehydes.

Entry ^a	Ketone	Product ^b	Time (min)	Yield (%)	m.p.(°C)		Ref.
					Found	Reported	
1a			40	85	Oil	Oil	[35a]
1b			50	83	72-74	72-74	[35a]
1c			180	15	Decomposed	Decomposed	[35a]
1d			40	95	Oil	Oil	[35a]
1e			40	88	54-56	54-56	[35a]
1f			36	70	Sticky oil	Oil	[38]
1g			30	80	165-170 (dec)	–	This work
1h			40	82	142-144	–	This work
1i			300	91	210-212	210-212	[38]
1j			700	85	100-102	98-100	[39]
1k			100	73	75-77	75-77	[35a]
1l			80	58	Oil	Oil	[35a]
1m			80	58	Oil	Oil	[35a]
1n			80	58	Oil	Oil	[35a]
1o			50	96	Oil	Oil	[35a]
1p			60	85	172-174	–	This work
1q		–	200	–	–	–	–

^aConditions: Ketone and aldehyde (1 mmol), CH₃CN (3 mL), ADSA-MNPs (0.01 g), 30% aq. H₂O₂ (1 mL, 9.8 mmol), reactions are carried out at rt.

^bThe structures of the products were established from their physical properties and spectral (¹H NMR, ¹³C NMR and IR) analysis and compared with the data reported in the literature and amount the peroxide is determined by iodometric titration.

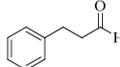
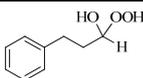
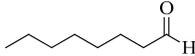
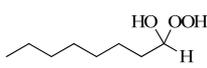
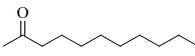
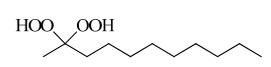
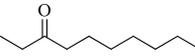
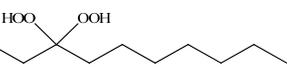
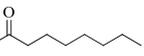
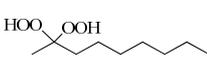
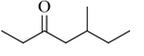
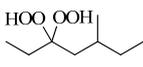
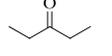
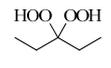
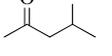
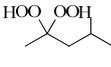
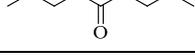
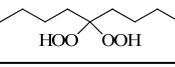
Table 3. Peroxidation of different cyclic ketones.

Entry ^a	Ketone	Product ^b	Time (min)	Yield (%)	m.p.(°C)		Ref.
					Found	Reported	
2a			7	98	Oil	Oil	[35a]
2b			10	95	Oil	Oil	[35a]
2c			15	93	64-66	60-61	[26]
2d			12	96	Oil	Oil	[8]
2e			23	85	138-140 (Decomposed)	137-138 (Decomposed)	[26]
2f			11	96	148-150	147-148	[26]
2g			10	92	Oil	Oil	[28]
2h			7	98	Oil	Oil	[28]

^aConditions: Ketone and aldehyde (1 mmol), CH₃CN (3 mL), ADSA-MNPs (0.01 g), 30% aq. H₂O₂ (1 mL, 9.8 mmol), reactions are carried out at rt.

^bThe structures of the products were established from their physical properties and spectral (¹H NMR, ¹³C NMR and IR) analysis and compared with the data reported in the literature and amount the peroxide is determined by iodometric titration.

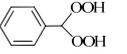
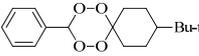
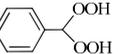
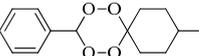
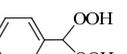
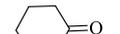
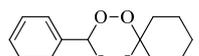
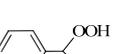
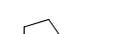
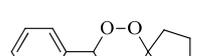
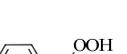
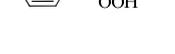
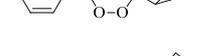
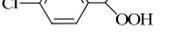
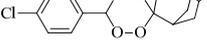
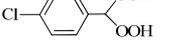
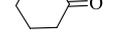
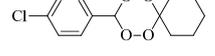
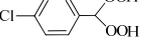
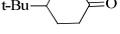
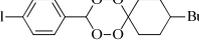
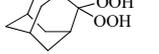
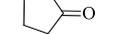
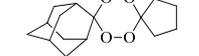
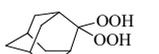
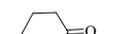
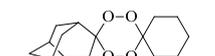
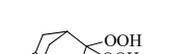
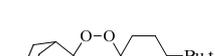
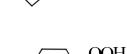
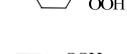
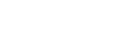
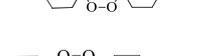
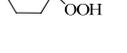
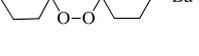
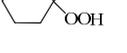
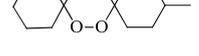
Table 4. Peroxidation of side chain aliphatic ketones and aldehydes.

Entry ^a	Ketone	Product ^b	Time (min)	Yield (%)	m.p.(°C)		Ref.
					Found	Reported	
3a			37	96	Oil	Oil	[35a]
3b			42	95	Oil	Oil	[35a]
3c			10	93	Oil	Oil	[26]
3d			9	92	31-33	30.1-30.5	[26]
3e			10	94	Oil	Oil	[35a]
3f			15	86	Oil	Oil	[26]
3g			7	95	Oil	Oil	[35a]
3h			8	94	Oil	Oil	[35a]
3i			12	93	Oil	Oil	[26]

^aConditions: Ketone and aldehyde (1 mmol), CH₃CN (3mL), ADSA-MNPs (0.01 g), 30% aq. H₂O₂ (1 mL, 9.8 mmol), reactions are carried out at rt.

^bThe structures of the products were established from their physical properties and spectral (¹H NMR, ¹³C NMR and IR) analysis and compared with the data reported in the literature and amount the peroxide is determined by iodometric titration.

Table 5. Synthesis of tetraoxanes using of *gem*-dihydroperoxides.

Entry ^a	<i>Gem</i> -dihydroperoxide	Ketone	Product ^b	Time (min)	Yield (%)	m.p.(°C)		Ref.
						Found	Reported	
4a				9	87	122-124	123-125	[37]
4b				12	87	101-103	101-102	[38]
4c				13	84	78-80	78-80	[38]
4d				14	85	73-75	73-75	[38]
4e				13	75	61-63	60-64	[37]
4f				15	72	73-75	70-72	[37]
4g				13	81	98-100	98-100	[38]
4h				8	84	114-116	114-116	[38]
4i				7	86	Oil	Oil	[37]
4j				9	85	58-62	55-58	[37]
4k				8	83	131-133	134-136	[37]
4l				5	90	191-193	190-192	[37]
4m				6	92	102-104	100-102	[37]
4n				7	87	86-88	86-88	[38]
4o				7	91	153-155	153-154	[38]
4p				8	89	70-72	70-72	[38]

^aConditions: *Gem*-dihydroperoxide (1 mmol), ketone (1 mmol), MeCN (3 ml), ADSA-MNPs (0.01 g), reactions are carried out at rt.

^bThe structures of the products were established from their physical properties and spectral (¹H NMR, ¹³C NMR and IR) analysis and compared with the data reported in the literature and amount the peroxide is determined by iodometric titration.

Table 6. Comparing reported results for peroxidation of cyclohexanone.

Entry	Catalyst	Amount of catalyst	Condition	Time (min)	Yield (%)	Ref
1	ADSA-MNPs	0.01 g	r. t	10	98	This work
2	Silica sulfuric acid	0.1 g	r. t	20	98	[35b]
3	Bi(OTf) ₃	5 mol%	r. t	18	78	[33]
4	phosphomolybdic acid	2 mol%	r. t	150	95	[32]
5	Re ₂ O ₇	5 mol%	r. t	30	79	[31]
6	CAN reagent	0.05 g	r. t	120	87	[28]
7	NaHSO ₄ ·SiO ₂	0.1 g	r. t	20	98	[30]

4. Conclusion

In conclusion, ADSA-MNPs were explored as a high active, easily available, reusable and non-toxic nanocatalyst towards the conversion of ketones and aldehydes to their corresponding *gem*-dihydroperoxides and 1,2,3,4-tetraoxanes. No complex procedures were required and all of the reactions proceeded smoothly with low reaction times at room temperature to furnish the titled products in high to excellent yields. The ADSA-MNPs catalyst exhibited a high reusability potential and showed no significant loss of activity after six consecutive runs (The yields were 98, 98, 96, 95, 95 and 94 % , respectively). This reusability of the catalyst makes the process less contaminant, cost-effective and environmentally friendly.

Acknowledgments

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