



The catalytic function of a silica gel-immobilized Mn(II)-hydrazide complex for alkene epoxidation with H₂O₂

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ARTICLE INFO

Article history:

Received 1 April 2011

Received in revised form 18 May 2011

Accepted 18 May 2011

Available online 27 May 2011

Keywords:

Catalytic epoxidation

Supported manganese(II) complex

Hydrazone Schiff base

Modified silica surface

Hydrogen peroxide

ABSTRACT

An efficient and highly selective heterogeneous catalyst was developed by immobilization of a manganese complex on an inorganic support to yield (silica gel)-O₂(EtO)Si-L¹-Mn(HL²) [(L¹)⁻ = modified salicylaldehydato and H₂L² = (E)-N'-(2-hydroxy-3-methoxybenzylidene)benzohydrazide]. Mn(II) has been anchored on the surface of functionalized silica by means of N,O-coordination to the covalently Si-O bound modified salicylaldehydato Schiff base ligand. The prepared material (silica gel)-O₂(EtO)Si-L¹-Mn(HL²), was characterized by elemental and thermogravimetric analyses (TGA and DTA), UV-vis and FT-IR spectroscopy. This new material is demonstrated to be a very active catalyst in clean epoxidation reactions using a combined oxidant of aqueous hydrogen peroxide and acetonitrile in the presence of aqueous sodium hydrogencarbonate. The effects of reaction parameters such as solvent, NaHCO₃ and oxidant in the epoxidation of *cis*-cyclooctene were investigated. Cycloalkenes were oxidized efficiently to their corresponding epoxide with 87–100% selectivity in the presence of this catalyst. This catalytic system showed also good activities in the epoxidation of linear alkenes. The obtained results show that this catalyst is a robust and stable heterogeneous catalyst which can be recovered quantitatively by simple filtration and reused multiple times without loss of its activity.

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1. Introduction

Epoxidation reactions with hydrogen peroxide, one of the 'greenest' terminal oxidants, are of great interest due to the importance of epoxides in the manufacture of both bulk and fine chemicals [1]. Epoxidation reactions that use hydrogen peroxide in conjunction with cheap, manageable and relatively non-toxic metal-based catalysts are potentially viable for large-scale production. However, good epoxidation catalysts must activate H₂O₂ without radical formation. Metal-catalyzed epoxidation of alkenes with hydrogen peroxide has been reviewed [2]. In agreement with the ever increasing environmental awareness, new oxidative processes based on the activation of H₂O₂ by robust, efficient and recyclable heterogeneous catalysts were developed [3,4]. Heterogeneous catalysts for epoxidations are attracting a lot of attention and are actively investigated because of advantages such as easy handling and product separation, catalyst recovery and less waste [5]. Among the various transition metals for heterogeneous catalytic epoxidation, manganese stands out as the most efficient, economical and environmental benign one. Various manganese

complexes immobilized on an inorganic matrix are known to be efficient and applicable as catalysts for the epoxidation of a wide range of alkenes [6]. Manganese porphyrin complexes have been extensively investigated as models for enzymes and used in catalysis with various single oxygen atom donors including H₂O₂ [7]. Alkene epoxidation reactions catalyzed by manganese complexes in homogeneous and heterogeneous media and the mechanism involved in these reactions are well established [8,9]. The mechanism of alkene epoxidation by manganese-based catalysts in the presence of bicarbonate was studied theoretically [10]. However, the development of efficient manganese systems that incorporate H₂O₂ has limitations due to competitive H₂O₂ dismutation by both the Mn center (catalase-type activity) and the inorganic support. These limitations can explain why only a few such systems, based on supported manganese catalysts and H₂O₂, have been reported for alkene epoxidation [11,12]. Castaman et al. employed a binuclear carboxylated bridged manganese complex immobilized on silica for epoxidation of alkenes [13]. This catalyst was able to epoxidize cyclohexene and cyclooctene with iodosylbenzene. With H₂O₂ and *tert*-butylhydroperoxide as oxidant in homogeneous and heterogeneous media, products were obtained in lower yields. Imidazole-based acetamide/Mn(II) systems [14,15] and acetylacetonate-based Schiff base/Mn(II) systems [16] have also been reported as homogeneous and heterogeneous catalysts for alkene epoxidation with H₂O₂.

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Mn(III) Schiff base complexes have been heterogenized by their covalent binding to organic polymers, encapsulation, entrapment, adsorption and covalent attachment to porous inorganic supports, such as zeolites, MCM-41 and clays [17,18]. Preparation of heterogeneous catalysts, by covalent immobilization of transition-metal complexes on silica surface represents one of the most usable approaches [19]. Many heterogeneous catalysts contain metal ions and chemically modified silica gels with active organic components [20]. Modified silica exhibits some advantages over modified resins such as high surface area, high thermal and chemical stability. Since the early 1990s and the advent of mesoporous silicas, the development of new solid catalysts and the heterogenization of homogeneous systems for oxidation processes have become very attractive topics. A major drawback of transition-metal catalysts coordinated to monodentate ligands is that they usually undergo leaching of the active species into solution, especially in the presence of protic agents such as alcohols or organic peroxides [21]. A simple way to minimize the leaching of the active ingredient is to anchor polydentate ligands onto the support surface, as this type of chelating system offers high coordinative stability for the catalytic ingredient.

Against this background, we investigate here the anchoring of a manganese(II) hydrazide Schiff base moiety onto a silica substrate functionalized with a polydentate salicylaldehyde ligand. The product of salicylaldehyde and benzhydrazide condensation has some similarities to non-symmetrical salen-type ligands. These types of hydrazone Schiff base complexes show considerable catalytic activities. The efficiency of homogeneous hydrazone based catalysts in alkene epoxidations [22,23] led us to the design of their heterogeneous analogues using silica as a support. This article describes the efficient and highly selective epoxidation of alkenes with 30% aqueous H₂O₂ in the presence of silica–Mn(II)–hydrazide Schiff base as a reusable solid catalyst.

2. Experimental

2.1. Materials and equipments

Silica gel (0.063–0.200 mm) and all other reagents were obtained from commercial sources (Merck or Fluka) and were used as received without further purification. Aqueous 30% hydrogen peroxide (8.12 mol/L) was used and its exact concentration was determined before use by titration with standard KMnO₄. (*E*)-*N*-(2-Hydroxy-3-methoxybenzylidene)benzohydrazide, H₂L², was synthesized according to a reported procedure [22]. ¹H NMR spectra were recorded by use of a Bruker 250 MHz, spectrometer. Elemental analyses were determined on a CHN Perkin-Elmer 2400 gas analyzer. IR spectra were recorded on a Perkin-Elmer 597 spectrometer. The solution and diffuse reflectance DR UV–Vis spectra in the range of 300–800 nm were measured on a CARY 5E spectrophotometer, with the spectra referenced to BaSO₄ (disk diameter 13 mm, thickness 2 mm). The manganese content of the final material was determined by ICP model ARL 3410, or alternatively, by a Varian spectrometer AAS-110. The reaction products of the oxidation were determined and analyzed by an HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m × 320 μm × 0.25 μm) with flame-ionization detector and gas chromatograph–mass spectrometry (Hewlett-Packard 5973 Series MS-HP gas chromatograph with a mass-selective detector).

2.2. Synthesis of *N*-(triethoxysilylpropyl)salicylaldimine [(EtO)₃Si–L¹H]

The linker was synthesized according to a reported procedure [24]. A solution of aminopropyltriethoxysilane (2.21 g, 10.0 mmol)

in methanol (10 mL) was added to a solution of salicylaldehyde (1.22 g, 10.0 mmol) in methanol (10 mL) and refluxed for 2 h. The colorless solution immediately turned yellow. The reaction was maintained in reflux for 2 h and then the solvent was removed under reduced pressure. The resulting viscous yellow oil was dissolved in dichloromethane and washed repeatedly with water. The organic layer was separated and dried over anhydrous magnesium sulfate followed by solvent evaporation and drying at room temperature for several hours. Yield 2.30 g, 71.0%. IR (KBr, cm⁻¹): 3449 (w) (O–H), 3065 (w), 2977 (vs), 2930 (s), 2894 (s), 2744 (w), 1634 (vs) (C=N), 1585 (m), 1498 (m), 1462 (m), 1391 (m), 1344 (w), 1281 (s), 1191 (w), 1167 (s), 1107 (vs), 1084 (vs), 959 (s), 899 (w), 871 (w), 795 (m), 758 (s), 641 (w), 568 (w), 526 (w), 465 (m). ¹H NMR (CDCl₃) δ = 0.604 (m, 2H, SiCH₂), 1.154 (t, ³J = 7.0 Hz, 9H, SiOCH₂CH₃), 1.742 (m, 2H, NCH₂CH₂), 3.473 (t, ³J = 6.75 Hz, NCH₂), 3.748 (q, ³J = 7.0 Hz, 6H, SiOCH₂), 6.722–7.212 (m, 4H, Ar), 8.190 (s, 1H, N=CH), 13.418 (s, 1H, Ar–OH) ppm.

2.3. Functionalization of silica gel to (silica gel)–O₂(EtO)Si–L¹H (**1**)

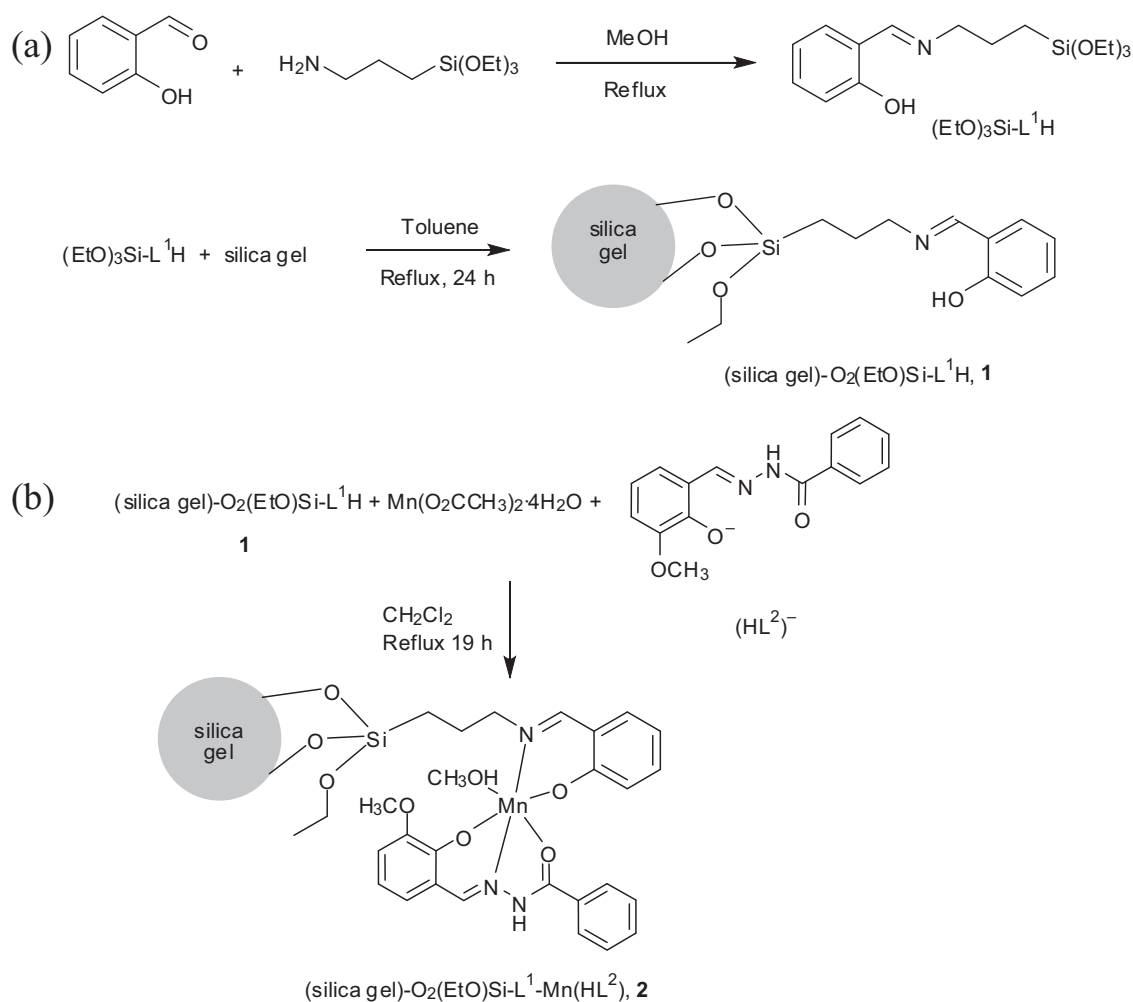
The *N*-(triethoxysilylpropyl)salicylalimine linker was anchored onto the silica surface via a grafting method. The procedure of synthesis was similar to the reported procedure with some modifications [25]. The amorphous silica gel was preliminary heated in an oven at 500 °C for 24 h to remove adsorbed water. A 5.0 g sample of the pretreated silica gel powder was suspended in 50 mL of dry toluene in a round bottomed flask (100 mL) which was flushed with N₂. (EtO)₃Si–L¹H (1.2 g, 3.7 mmol) was then added and the suspension stirred for 24 h under reflux at N₂ atmosphere. The resulting suspension was filtered and washed with Et₂O (3 × 15 mL). The recovered powder was extracted in a Soxhlet using refluxing CH₃OH (750 mL) for 24 h. The functionalized silica gel, designated as (silica gel)–O₂(EtO)Si–L¹H, was dried under vacuum at room temperature for 18 h. A yellow powder was recovered. IR (KBr, cm⁻¹): 3444 (m, br), 2935 (w), 2864 (w), 1647 (m), 1101 (vs, br), 813 (m), 473 (s).

2.4. Immobilization of the manganese complex to (silica gel)–O₂(EtO)Si–L¹–Mn(HL²) (**2**)

Mn(O₂CCH₃)₂·4H₂O (20 μmol, 0.005 g) and H₂L² (19 μmol, 0.005 g) were dissolved in 30 mL of dichloromethane. The functionalized silica gel (silica gel)–O₂(EtO)Si–L¹H (2.0 g) was then added to the solution and the mixture stirred under reflux for 24 h followed by Soxhlet extraction with CH₃OH for 24 h. The green material was dried under vacuum overnight, yielding 1.840 g. Most of the (silica gel)–O₂(EtO)Si–L¹–Mn(HL²) was found lost in the Soxhlet extraction since the cleaning of the Soxhlet timble was difficult. CHN analyses showed the presence of both L¹ and L². In order to confirm that the Mn is indeed bound as L¹–Mn–L² and not (at least to some extent) as L¹–Mn–L¹ from two neighboring L¹-groups, the UV–vis spectra of the compounds (silica gel)–O₂(EtO)Si–L¹H (**1**) and (silica gel)–O₂(EtO)Si–L¹–Mn(HL²) (**2**) were compared with its homogeneous analogues (not shown). IR (KBr, cm⁻¹): 3443 (br, w), 3217 (w), 3075 (w), 2935 (w), 2858 (w), 1617 (m), 1574 (m), 1442 (m), 1216 (s), 1085 (vbr, vs), 808 (s), 741 (w), 712 (w), 740 (vs).

2.5. General procedure for the epoxidation of alkenes

The epoxidation of alkenes with hydrogen peroxide was performed in a 25-mL round-bottom flask. In a typical experiment, the flask was charged with 3.0 mL of CH₃CN, 1.0 mmol alkene, 1.0 mmol NaHCO₃, 0.1 g chlorobenzene as internal standard and



Scheme 1. (a) The modification of the silica gel surface by organo-silane to (silica gel)-O₂(EtO)Si-L¹H (**1**), (b) immobilization of Mn(II) on the surface of functionalized silica gel to give compound **2**.

0.01 g (silica gel)-O₂(EtO)Si-L¹-Mn(HL²) (**2**) as supported catalyst. To this mixture, 4.0–10 mmol of 8.12 mol/L aqueous solution of hydrogen peroxide was added. The reactant mixture was stirred vigorously for 5 h at room temperature. At appropriate intervals, aliquots were removed and analyzed immediately by GC. The activity of bare silica gel (with no conversion) and functionalized silica gel **1** (conversion 13.5%) was also measured in the absence of Mn(II). Conversions with (silica gel)-O₂(EtO)Si-L¹H were very much lower than the conversion in the presence of the Mn-containing catalyst. The reaction products were quantified by gas chromatography and identified by comparison with the retention time and spectral data to those of an authentic sample. Alkene conversion (%) and oxidation products yields based on the starting substrate were quantified by comparison with chlorobenzene.

In some instances, reactions were carried out on a larger scale and the epoxides were isolated as further confirmation of identity and yield by NMR.

For Mn leaching test in the oxidation of cyclooctene, after 4 h the solid catalyst **2** was removed from the reaction mixture by centrifugation. The supernatant was decanted, 2 mL concentrated H₂SO₄ added and then it was refluxed for 2 h. The resulting solution was investigated by atomic absorption spectrometry for traces of manganese.

3. Results and discussion

3.1. Synthesis and characterization of heterogeneous (silica gel)-O₂(EtO)Si-L¹H (**1**) and (silica gel)-O₂(EtO)Si-L¹-Mn(HL²) (**2**)

Salicylaldimine (salicylaldiminepropyltriethoxysilane) (EtO)₃SiCH₂CH₂CH₂N=C-C₆H₅(OH) was synthesized by condensation of aminopropyltriethoxysilane and salicylaldehyde in methanol. IR and ¹H NMR spectra of [(EtO)₃Si-L¹H] (Supplementary Information Figs. S1 and S2) confirm that the reaction of the organosilane with the salicylaldehyde occurs only by the Schiff condensation between the C=O and the NH₂ groups. Silica gel was grafted with the salicylaldimine group by treating it with (EtO)₃SiCH₂CH₂CH₂N=C-C₆H₅(OH) in refluxing toluene. The salicylaldimine group attached to the silica surface by condensation of silanol and ethoxy groups (Scheme 1a). The IR spectrum of the functionalized silica is shown in Fig. 1b. The characteristic organosilane and imine group vibrations (2935 and 1647 cm⁻¹, respectively) in the FT-IR spectra of the grafted material confirmed the presence of the salicylaldimine group on the surface of the silica. The results of carbon and nitrogen analyses of functionalized silica are compiled in Table 1. The observed C to N ratio of 9.07 matches the theoretical value of 10.29 with a similar error as in

Table 1
Elemental analyses of functionalized silica gel before and after Mn loading and chemical compositions of functionalized silica gel (fsg).

Material	C (%)	H (%)	N (%)	Mn (%)	mmol Imine/g fsg ⁻¹	mmol Mn/g fsg ⁻¹	mol Mn /mol imine ⁻¹
1	7.53	0.92	0.83	–	0.52	–	–
2	5.21	0.93	0.55	0.05	0.52	0.01	0.02

another reported study [26]. Furthermore, the amount of grafted imine (Table 1) shows that the salicylaldehyde loading in (silica gel)–O₂(EtO)Si–L¹H was 0.52 mmol imine/g of silica gel.

3.2. Preparation of supported catalyst

The hydrazone Schiff base complex of Mn(II) was immobilized on silica gel by refluxing manganese(II) acetate, H₂L² and (silica gel)–O₂(EtO)Si–L¹H (**1**) in dichloromethane (Scheme 1). H₂L² acts as a monoanionic tridentate ligand and coordinated through the deprotonated hydroxyl group, azomethine nitrogen and amide oxygen groups to Mn(II) [23]. The immobilization of Mn²⁺ on the surface of the (silica gel)–O₂(EtO)Si–L¹H occurs by means of chemical bonding with the imine nitrogen and deprotonated oxygen of phenol moiety groups of **1** as is shown in Scheme 1b. The prepared heterogeneous (silica gel)–O₂(EtO)Si–L¹–Mn(HL²) (**2**) catalyst was thoroughly washed with CH₃OH in order to eliminate Mn(HL²) species adsorbed on the support. The IR spectrum of the heterogeneous catalyst **2** (Fig. 1c) displays the characteristic bands associated with the N–H (3217 cm⁻¹) and C=O (1617 cm⁻¹) bonds of the amide functionality present in the (HL²)⁻ Schiff base ligand coordinated to Mn(II) [22]. The presence of an N–H broad band in **2** proves that the amide functionality exists and is not deprotonated. The IR spectrum of ligand H₂L² displays a C=O band at 1650 cm⁻¹ [22]. After complexation, it is shifted to lower wavenumber (1617 cm⁻¹) and this finding supports involvement of C=O in coordination to the manganese ion. Microanalyses confirmed, the anchored Mn(HL²). The UV–vis spectrum (Fig. 2) and TGA experiment (Fig. 3) suggested that the Mn(HL²) moiety was grafted onto the support. The absorption spectra of the solids **1** and **2** in BaSO₄ pellets are shown in Fig. 2. The spectra of **1** and **2** showed similar features due to the presence of the same aryl, aryl-O and imine functional groups. In the spectrum of **1** the bands at 224 and 249, 273, 311 and 400 nm could be attributed to the intraligand transitions of the salicylaldehyde ligand. In the spectrum of **2** the very similar bands could be attributed to the intraligand transitions of salicylaldehyde and hydrazone Schiff base ligands. Usually charge transfer bands which are allowed transitions are of higher intensity. However, for Mn(II) which is d⁵ high spin there can be no

spin-allowed d–d transitions and on the absorbance scale, the spin-forbidden d–d transitions cannot be seen. So the bands at 539, and 590 nm may be assigned to the metal to ligand charge transfer [27]. Further investigation using TGA/DTA showed that the pre-catalyst (silica gel)–O₂(EtO)Si–L¹–Mn(HL²) lost 8% of its weight up to 700 °C (Fig. 3), with the decomposition of the organic salicylaldehyde and the hydrazone Schiff base to leave SiO₂. The exothermic DTA peaks can be attributed to the decomposition of salicylaldehyde and the Schiff base ligand.

The experimental findings that support the presence of manganese in **2** as Mn(II) are as follows: (i) in the IR spectrum of (silica gel)–O₂(EtO)Si–L¹–Mn(HL²) (**2**) (Fig. 1c) N–H stretching vibration of H₂L² is clearly seen at 3217 cm⁻¹. It proves that in the compound **2**, H₂L² coordinates in the keto form as a tridentate monoanionic ligand. (ii) The N–H vibration of H₂L² is also seen at 3208 cm⁻¹ for a homogeneous analogue of compound **2** (Fig. S2). (E)-2-((Propylimino)methyl)phenol was used as homogeneous analogue of (silica gel)–O₃Si–L¹H and its Mn complex synthesized in the presence of the hydrazone-Schiff base (H₂L²) as a homogeneous analogue of the compound **2**. (iii) Furthermore, the EPR spectrum confirmed the presence of Mn(II) in the compound **2** (Fig S6).

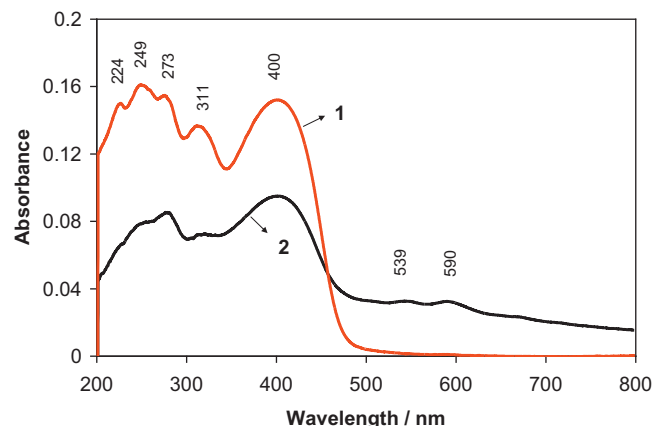


Fig. 2. Reflectance electronic spectra of the solids (silica gel)–O₂(EtO)Si–L¹H (**1**) and (silica gel)–O₂(EtO)Si–L¹–Mn(HL²) (**2**) in BaSO₄ pellets.

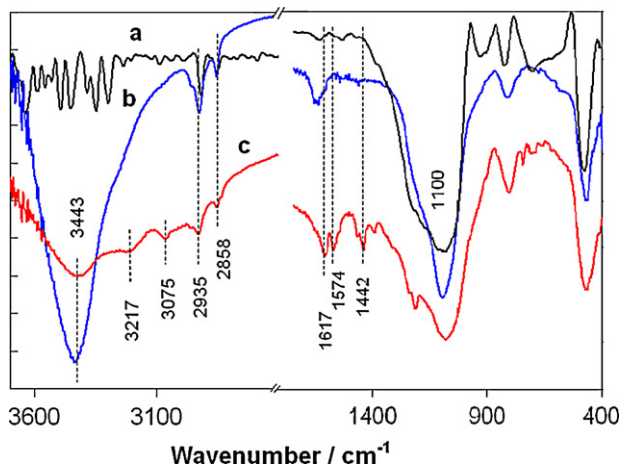


Fig. 1. FT-IR spectra of (a) dried silica gel, (b) (silica gel)–O₂(EtO)Si–L¹H (**1**) and (c) (silica gel)–O₂(EtO)Si–L¹–Mn(HL²) (**2**).

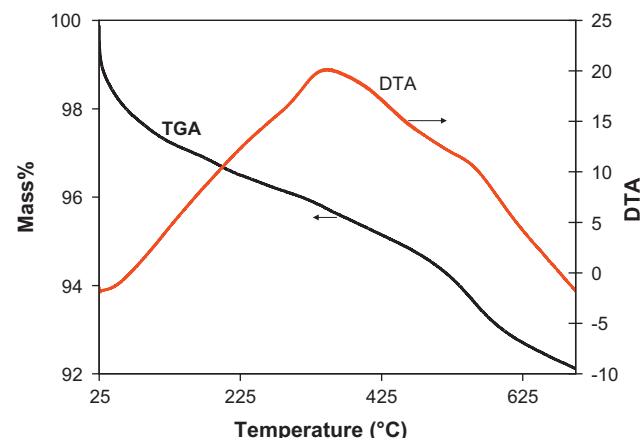


Fig. 3. TGA and DTA curve of (silica gel)–O₂(EtO)Si–L¹–Mn(HL²).

Table 2
Catalytic oxidation of cyclooctene with H₂O₂.^a

Entry	Catalyst	Additive	H ₂ O ₂	Conversion (%)
1	2	NaHCO ₃	–	0
2	2	–	H ₂ O ₂	0
3	2	Et ₃ N	H ₂ O ₂	20
4	2	NaHCO ₃ ^b	H ₂ O ₂	86
5	–	NaHCO ₃ ^c	H ₂ O ₂	12
6	Silica gel	NaHCO ₃ ^c	H ₂ O ₂	0
7	1	NaHCO ₃ ^b	H ₂ O ₂	13.5
8	MnCl ₂ (water free)	NaHCO ₃ ^b	H ₂ O ₂	0
9	Mn(CH ₃ CO ₂) ₂ ·4H ₂ O	NaHCO ₃ ^b	H ₂ O ₂	0

^a Condition: catalyst **2** 0.010 g, cyclooctene 1 mmol, CH₃CN 3 mL, H₂O₂ 10 mmol, and time 5 h at room temperature.

^b NaHCO₃ 5.5 mmol (0.46 g) and time 5 h at room temperature.

^c NaHCO₃ 1 mmol or NaHCO₃ 5.5 mmol, and time 5 h at room temperature.

A *g*-value of 2.05 was calculated which is close to Mn²⁺ whose *g*-value is 2.00.

3.3. Catalytic activity studies

3.3.1. Catalytic properties of immobilized Mn(II) in oxidation of cyclooctene

Hydrogen peroxide is a widely used oxidant with high active oxygen content [28], but it is a rather slow oxidizing agent in the absence of activators. According to some reports the addition of some alkaline species (e.g., NaOH, KOH, NaHCO₃) into the reaction system was beneficial to epoxide formation [29,30]. The oxidation of cyclooctene catalyzed by (silica gel)–O₂(EtO)Si–L¹–Mn(HL²) (**2**) was carried out with hydrogen peroxide as oxidant to give cyclooctene oxide as the sole product. Results of control experiments revealed that the presence of oxidant, sodium bicarbonate and catalyst were essential for the oxidation. Without either H₂O₂, NaHCO₃ or using silica gel instead of **2** no conversion was observed (Table 2, entries 1, 2 and 6, respectively). An additive like imidazole was not effective in cyclooctene oxidation (not shown in Table 2). However, addition of a base like triethylamine (Et₃N) increased the pH of the moderately acidic medium of H₂O₂ and conversion of 20% was observed for cyclooctene (Table 2, entry 3). The highest conversion of cyclooctene was achieved in the presence of NaHCO₃ (Table 2, entry 4). With NaHCO₃ and H₂O₂ alone an oxidation of up to 12% was observed (Table 2, entry 5) [31]. The silica gel support (unmodified, no metal loading) with NaHCO₃ and H₂O₂ did not show any catalytic activity (Table 2, entry 6). In the absence of manganese but with (silica gel)–O₂(EtO)Si–L¹H (**1**) some oxidation was observed (13.5%) probably due to the basic nature (Table 2, entry 7), similar to the reaction with NaHCO₃ and H₂O₂ alone. Bare Mn(II) ions did not activate H₂O₂ for alkene oxidation (Table 2, entries 7 and 8).

In search of suitable reaction conditions to achieve the maximum oxidation of cyclooctene, the effects of oxidant (moles of H₂O₂ per moles of cyclooctene) and bicarbonate concentrations and solvent of the reaction were studied.

3.3.2. Sodium bicarbonate effect

To understand the effect of the presence of NaHCO₃ in more detail, catalytic experiments with different amounts of NaHCO₃ as an additive were performed at 25 °C, catalyzed by the heterogeneous material **2**. The molar ratio of NaHCO₃ to alkene (cyclooctene) was varied from 0.05 to 5.5. The results of these studies are depicted in Fig. 4. A comparative experiment without NaHCO₃ gave no product (Table 2, entry 2). Increasing the molar ratio NaHCO₃:cyclooctene from 0.05 to 0.62 significantly accelerates the epoxidation rate within the first hour. At higher ratios of 1 and 5.5 the rate slows down again during the first hour. For longer reaction times between 1 h and 4 h there is no unifying trend. Clearly molar

Table 3
Solvent effect on the epoxidation of cyclooctene by **2**/NaHCO₃/H₂O₂.^a

Entry	Solvent	Conversion (%)	Selectivity (%)
1	<i>n</i> -Hexane	0	100
2	CH ₂ Cl ₂	7	100
3	Acetone	18	100
4	CH ₃ CH ₂ OH	20	100
5	CH ₃ OH	54	100
6	CH ₃ CN	92	100

^a Conditions: catalyst **2** 0.010 g, cyclooctene 1.0 mmol, solvent 3.0 mL, H₂O₂ 10.0 mmol, NaHCO₃ 1.0 mmol, and time 5 h and temperature 25 ± 1 °C.

ratios above 0.5 are advantageous to reach conversions around and above 80% after 5 h. The maximum conversion of cyclooctene was 92% for the NaHCO₃:cyclooctene ratio of 1. However, a further increase of the ratio to 5.5 did not increase the conversion any further after 5 h. That is probably due to the abrupt pH change of the solution.

It is pertinent to mention that sodium bicarbonate has been rarely used as a co-catalyst in a heterogeneous catalytic system in the presence of dilute aqueous H₂O₂ as oxidant [5]. Interestingly, NaHCO₃ alone can produce epoxide with low yield (Table 2, entry 5). This shows that the epoxidation reaction with **2**/H₂O₂ is catalytic in the presence of bicarbonate (Table 2, entry 4). With transition-metal catalysts bicarbonate activated H₂O₂ shows enormous efficiency of epoxidation compared to H₂O₂ alone, because of the formation of peroxymonocarbonate (HCO₄[–]) [31], which is a more reactive nucleophile than H₂O₂ and speeds up the reaction.

When the alkene reaction was carried out in the mildly acidic medium of H₂O₂ in the absence of NaHCO₃, no epoxide was formed for cyclooctene as a representative case (Table 2, entry 2). The role of NaHCO₃ in these reactions is to activate hydrogen peroxide by pH adjustment into the alkaline regime or by peroxymonocarbonate formation. To discriminate between these two functions of NaHCO₃, Et₃N was used instead of NaHCO₃ (Table 2, entry 3). Oxidation of cyclooctene was achieved but the conversion was lower than with **2**/NaHCO₃ and the acetamide product was not formed. We may conclude that NaHCO₃ adjusts the pH and also participates directly in the epoxidation. Since epoxidation in the presence of catalyst **2** increased remarkably, we may conclude that an active epoxidizing species is formed from the interaction of the Mn(II) complex and percarbonate.

3.3.3. Solvent effect

The catalytic efficacy of **2** was studied in different solvents. Table 3 illustrates the influence of the solvent nature in the

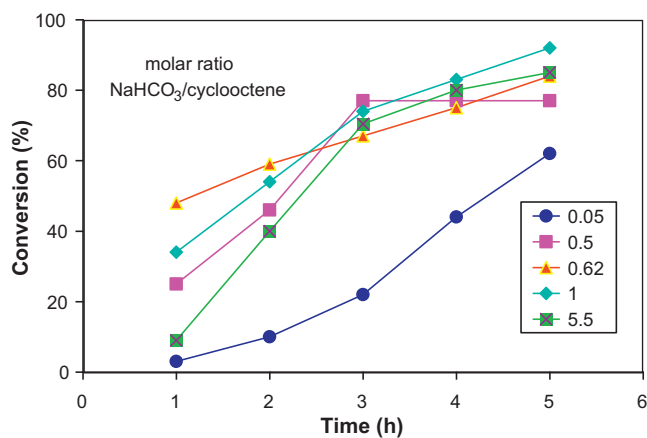


Fig. 4. The influence of the molar ratio NaHCO₃ to cyclooctene in the epoxidation of cyclooctene with hydrogen peroxide catalyzed by **2**. Conditions: catalyst **2** 0.010 g, cyclooctene 1.0 mmol, CH₃CN 3 mL, and H₂O₂ 10 mmol at 25 ± 1 °C.

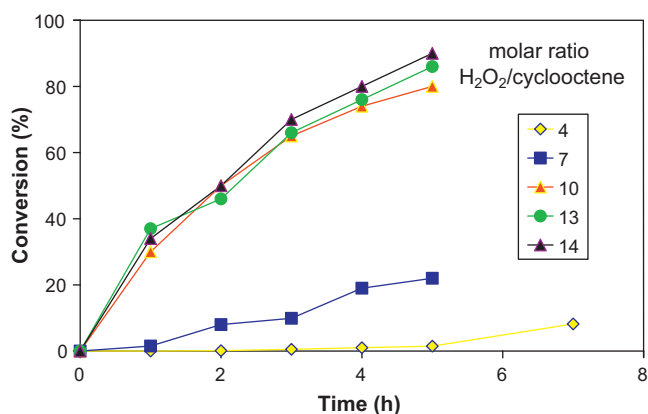


Fig. 5. Effect of the molar ratio H_2O_2 to cyclooctene in the epoxidation of cyclooctene by **2**. Conditions: catalyst **0.010 g**, cyclooctene **1.0 mmol**, CH_3CN **3 mL**, and NaHCO_3 **1.0 mmol** at $25 \pm 1^\circ\text{C}$.

catalytic epoxidation of cyclooctene by **2**. It was observed that the catalytic activity of (silica gel)- $\text{O}_2(\text{EtO})\text{Si-L}^1\text{-Mn}(\text{HL})^2$ decreases in the order acetonitrile (dielectric constant $\epsilon/\epsilon_0 = 37.5$ where ϵ_0 is the electric permittivity of free space) > methanol (32.7) > ethanol (26.6) > acetone (20.7) > dichloromethane (8.9) > *n*-hexane (1.88) at a temperature of 25°C . Dichloromethane and hexane are not miscible with aqueous H_2O_2 which could also be the reason for low catalytic efficiency in these cases. The best performance of the catalyst was observed in acetonitrile. The high conversion in acetonitrile is possibly due to its dielectric constant ($\epsilon/\epsilon_0 = 37.5$) and dipole moment ($\mu = 3.90\text{D}$) which are the highest of all the solvents used. The optimum polarity of acetonitrile helps to dissolve both the alkene and H_2O_2 which facilitates the epoxidation reaction in this solvent. Furthermore, the large improvement in the cyclooctene conversion (Table 3) with changing the solvent from methanol (54%) to acetonitrile (92%) suggests the involvement of acetonitrile in the oxidation. This plausible reaction pathway was confirmed by observing acetamide in the GC analyses and ^1H NMR spectra of all the alkene oxidation products. Peroxycarboximide acid is formed in situ by reaction of hydrogen peroxide and acetonitrile in the presence of NaHCO_3 . Strong bases such as NaOH and KOH catalyze the epoxidation of alkenes using hydrogen peroxide in the presence of nitriles in a strong alkaline medium [32].

3.3.4. Effect of H_2O_2 /cyclooctene ratio

We have monitored the progress of cyclooctene epoxidation for different molar ratios of oxidant and substrate (Fig. 5). Molar ratios H_2O_2 /cyclooctene of 1.5, 4, 7, 10, 13 and 14 were considered while keeping the fixed amount of cyclooctene (1.0 mmol) and catalyst **2** (0.01 g) in 3 mL of acetonitrile at $25 \pm 1^\circ\text{C}$. It was found that at a ratio of oxidant:alkene of 4 no conversion occurred and at a ratio of 7 the conversion of cyclooctene was only 25%. This findings support slow decomposition of hydrogen peroxide by **2**. Increasing the H_2O_2 /cyclooctene ratio from 7 to 10 increased the conversion from 25% to 86%. Further increase resulted not in a remarkable increase of the conversion. So the H_2O_2 /cyclooctene ratio of 10 was selected as an optimized ratio for further studies. An excess of oxidant of this order is documented for epoxidation reactions in the literature [31,33]. Notably, no induction period was observed in any of the reactions.

Epoxide was not the sole product in the oxidation of cyclooctene catalyzed by metal complexes in homogeneous medium. Along with the desired epoxide, cyclooctane-1,2-diol was also generated [34]. Oxidation of cyclooctene was studied over Mn(II) Schiff base intercalated montmorillonite clay catalysts using 30% H_2O_2 as oxidant which shows a conversion of ca. 58% [35]. Epoxide con-

Table 4

Recycling studies with catalyst **2** in the oxidation of cyclooctene by hydrogen peroxide after 5 h of reaction time.^a

Entry	No. recycle	Conversion (%)	Selectivity (%)
1	0	90	100
2	1	89	100
3	2	92	100
4	3	91	100
5	4	88	100
6	5	86	100
7	6	87	100
8	7	86	100
9	8	88	100
10	9	86	100

^a Conditions: catalyst **2** 0.01 g, cyclooctene 1.0 mmol, CH_3CN 3 mL, and H_2O_2 10 mmol at $25 \pm 1^\circ\text{C}$. Conversion was based on the starting alkene.

version in this reaction improves (to 85%) on intercalation of the Mn(II)-salen complex into montmorillonite K-10 [36]. In the latter case, iodosylbenzene (PhIO) was used as oxidant. Recycling of the catalysts could not be realized if PhIO is used, because it was impossible to completely free the catalyst from PhIO_2 , a disproportionation product of PhIO [37].

3.4. Catalyst recycling

In order to investigate the possibility of several recycling runs for **2**, the solid catalyst was separated from the reaction mixture by centrifugation. The supernatant was decanted, and then the solid catalyst was washed two times by adding acetonitrile and centrifugation. The used and washed catalyst was transferred to a flask and used again in a fresh reaction. The catalyst was recycled nine times for cyclooctene epoxidations. In general, no substantial loss in the catalytic activity of the immobilized catalyst was observed compared with that of a fresh sample, as shown in Table 4. Therefore, recycling is possible in the case of **2**.

3.5. Catalyst stability

Catalyst stability is of major concern in homogeneous and heterogeneous catalysis. In the present case, for the system studied herein two phenomena were screened in detail:

- Leaching of the Mn(II)-complexes from the SiO_2 support: This was tested by the 'filtration method' according to reported procedure [5]. Accordingly, in a typical catalytic oxidation of cyclooctene, after 2 h (conversion 30%), the solid catalyst was filtered. The progress of the oxidation reaction in the filtrate was monitored by GC. Our data showed that, no evolution of the studied reactions was observed in the filtrate after 5 h (conversion 38%). The 8% increase in the conversion of cyclooctene relates to the oxidation in the absence of the catalyst as was seen in Table 2 (entry 3). The absence of Mn in the solution through leaching of **2** was also studied (see Section 2.5 for details) by measuring manganese ion in solution. The investigation of the resulting solution by atomic absorption method showed no detectable (<0.02 ppm) manganese. This ensured that no leaching of the active supported Mn(II)-components occurred. Thus, the obtained catalytic results derive exclusively from the heterogeneous catalyst.
- Leaching of free Mn ions into solution: The catalytic performance of the manganese salts MnCl_2 and $\text{Mn}(\text{CH}_3\text{COO})_2$ as homogeneous catalysts was examined. For comparison the data are provided in Table 2 (entries 8 and 9). As shown in Table 2 the manganese salts in CH_3CN solution showed no catalytic activity in the oxidation of cyclooctene with 30% H_2O_2 since hydrogen peroxide was decomposed instantly in the first

Table 5
Oxidation of various alkenes with **2**/NaHCO₃/H₂O₂/CH₃CN.^a

Entry	Alkene	Conversion (%) ^b	Product(s)	Selectivity (%)	TOF (h ⁻¹) ^c
1		63		>99	1260
2		92		>99	1840
3		98		87	1960
				13	
4		92		60	1840
				31	
5		83		93	1660
				7	
6		93		>99	1860
7		97		>99	1940
8		13 ^d		>99	130
9		32 ^d		47 ^c	320
				53 ^c	
10		15 ^d		>99	150

^a Conditions: catalyst **2** 0.01 g, alkene 1 mmol, CH₃CN 3 mL, H₂O₂ 10 mmol, NaHCO₃ 1.0 mmol and time 5 h at room temperature.

^b Conversion based on starting alkene and GC analysis; selectivity from GC analysis, unless noted otherwise under *d*.

^c TOF: turnover frequency = the catalytic turnover per unit time. TON: turnover number = number of moles of product formed per mole of Mn in the catalyst.

^d Substrate 0.5 mmol, products were determined by ¹H NMR.

minutes of the reaction. Overall, the control experiments provide evidence that the observed catalytic results are derived by the heterogeneous catalyst and no leaching of the active component or demetallation occurs during the catalytic process. Leaching of Mn may be cannot be excluded strictly but that (silica gel)-O₂(EtO)Si-L¹-Mn(HL²) system may, thus, serve as a basin or a source of continuous Mn supply in low concentration (so to avoid too rapid H₂O₂ decomposition).

Heterogeneous Mn(II) catalysts with acetylacetonate-based Schiff base ligands have been reported for alkene epoxidation with

H₂O₂/CH₃COONH₄ [35]. However, they are not stable and after a first use of the heterogeneous catalysts, they lost their catalytic activities. A Mn(III)-salen complex immobilized into pillared clays was applied in the heterogeneous epoxidation of styrene with PhIO [38]. It was not very stable and leaching and deactivation occurred.

The only drawback of the **2**/NaHCO₃/H₂O₂/CH₃CN system is the need for a 10-fold excess of hydrogen peroxide relative to substrate. The excess consumption of H₂O₂ is attributed to the competitive parallel reaction of hydrogen peroxide decomposition promoted by the catalyst **2**. This situation has been also reported for Mn(III)

and Mo(IV)–salen complexes immobilized on mesoporous silica gel [39].

3.6. Oxidation of other acyclic/aliphatic and cyclic alkenes

The results of the catalytic epoxidation of different alkene substrates are summarized in Table 5. Oxidation of various alkenes was performed under the same reaction conditions which proved to be the best for cyclooctene ($\text{H}_2\text{O}_2/\text{cyclooctene}$ ratio = 10, NaHCO_3 1 mmol, acetonitrile 3 ml and reaction temperature 25 °C). The heterogeneous catalytic system **2** was able to oxidize linear oct-1-ene to the corresponding epoxide with good yield, 63% (Table 5, entry 1) and excellent selectivity. Cyclohexene gave the corresponding epoxides as the main product with 87% selectivity (Table 5, entry 3). This result is similar to the oxidation of cyclohexene by a homogeneous Mn(II)–hydrazone catalyst/PhIO/imidazole/ CH_3CN system [22]. Cyclohexene is more prone to both epoxidation and allylic oxidation [40]. To provide evidence for or against a non-radical mechanism and to evaluate the catalyst selectivity, oxygenation of cyclohexene was performed. Norbornene gave *exo*- and *endo*-norbornene oxide with 60 and 30% selectivity, respectively (Table 5, entry 4). This is in contrast to the reported layered hydroxalcalite ($\text{Mg}_{10}\text{Al}_2(\text{OH})_{24}\text{CO}_3$)/ H_2O_2 /benzotrile/ CH_3OH system that gives only *exo*-norbornene oxide [33]. Remarkably, α -methyl styrene was oxidized to give α -methyl styrene oxide in 77% yield and 6% acetophenone without formation of benzaldehyde (Table 5, entry 5). Oxidation of 1,3-cyclooctadiene resulted in the monooxide product (*Z*)-9-oxabicyclo[6.1.0]non-2-ene (Table 5, entry 7). Apparently, the presence of an electron withdrawing epoxide group allows the oxidation to proceed further. The epoxidation of *trans*-stilbene proceeded stereospecifically with retention of configuration at the double bonds (Table 5, entry 9). In oxidation of *cis*-stilbene a mixture of *cis*- and *trans*-stilbene oxide with 1:1.11, molar ratio was obtained (Table 5, entry 11). This result showed that oxygen transfer to alkene is not concerted and that it goes through a radical intermediate. The radical intermediate can be transferred to *cis*-epoxide via direct collapse or there is a rotation of the radical intermediate which then collapses to *trans*-epoxide [41]. In the epoxidation of *cis*- and *trans*-stilbenes the steric effects were distinct. The sterically demanding *trans*-stilbene is less reactive than the *cis* isomer. Typical epoxidizing reagents such as peroxyacids have been shown to react with *cis* alkenes about two times faster than the corresponding *trans* alkenes [42]. For *m*-chloroperoxybenzoic acid in methylene chloride at room temperature, *cis*- and *trans*-stilbenes are epoxidized at equal rates. The low yields of *trans*-stilbene and phenanthrene were due to their solubility problem in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (from 30% hydrogen peroxide) solvent mixture (Table 5, entries 8–10). If all the studied alkenes were considered, reactivity and epoxide selectivity of **2**/ $\text{NaHCO}_3/\text{H}_2\text{O}_2/\text{CH}_3\text{CN}$ system is very similar to the reported homogeneous Mn(TPP)OAc/imidazol/ $\text{NaHCO}_3/\text{H}_2\text{O}_2/\text{CH}_3\text{CN}$ system (TPP = tetraphenylporphyrine) [43].

Various heterogeneous catalysts of Mn(II)/Mn(III) and Mg have been used for the oxidation of cyclooctene, cyclohexene, and *cis*-stilbene with H_2O_2 [9,14,33,44–48] (see Supplementary Information Table S1 for summary of comparison results). None of the catalysts show high activity and epoxide selectivity like the (silica gel)– $\text{O}_2(\text{EtO})\text{Si}-\text{L}^1-\text{Mn}(\text{HL}^2)$ catalyst **2**. The layered hydroxalcalite, $\text{Mg}_{10}\text{Al}_2(\text{OH})_{24}\text{CO}_3$, acts as an efficient base catalyst for the epoxidation of various alkenes using hydrogen peroxide in the presence of benzonitrile [33] but the catalyst works at higher temperature than room temperature and the reaction needs more time (24 h) to be complete. This catalyst is also not recyclable. In addition to its excellent epoxide selectivity and very good conversion the **2**/ H_2O_2 system is very stable and can be recycled more than 10 times.

Mn(V)-oxo species are often viewed as active oxygen transfer agents capable of selective alkene epoxidation [49,50]. Considering the oxidation products of various alkenes, specially cyclohexene and *cis*-stilbene, a possible mechanism for the oxidation of alkenes by **2**/ $\text{NaHCO}_3/\text{H}_2\text{O}_2/\text{CH}_3\text{CN}$ system is metal based radical active species in addition to $\text{Mn}=\text{O}$ which is well known for selective epoxidation of alkenes.

4. Conclusion

We have developed an efficient heterogeneous catalyst system utilizing (silica gel)– $\text{O}_2(\text{EtO})\text{Si}-\text{L}^1-\text{Mn}(\text{HL}^2)$ (**2**) for epoxidation with a combined oxidant of aqueous hydrogen peroxide and acetonitrile. Good conversion with excellent selectivity was achieved in the case of cycloalkenes. The solid catalyst material **2** was easily separated from the reaction mixture via filtration, which made the work-up procedure simple. The catalyst **2** was reused in several catalytic runs without significant loss of activity. This system could be useful for many base-catalyzed selective oxidations. Thus, our experimental data revealed that NaHCO_3 could work very efficiently as a co-catalyst in the presence of the immobilized heterogeneous catalyst. This could open new application areas in heterogeneous catalytic oxidation systems in the future. The efficiency of homogeneous hydrazone based catalysts in alkene epoxidations is also seen in the heterogenized hydrazone based catalysts.

Acknowledgement

Authors are thankful to Zanjan University for financial support of this study.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.05.014.

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