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Short Communication

Synthesis and characterization of SBA-polyperoxyacid: An efficient heterogeneous solid peroxyacid catalyst for epoxidation of alkenes

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ABSTRACT

SBA-propy-3-allyl-imidazolium chloride (SBA-Im-Allyl) was easily prepared by nucleophilic substitution of SBA-propylchloride (SBA-Cl) with imidazole and then quaternization with allyl chloride. Then, a novel solid polyperoxyacid was synthesized by anchoring and oxidation of polyacrylic acid onto the surface of SBA-Im-Allyl. FT-IR, SEM, TGA–DTG and BET have been used to characterize the solid polyperoxyacid. This new catalyst did not leach from the support and can be recycled by treatment with hydrogen peroxide solution, and also loading of the catalyst was measured by iodometric titration. The solid polyperoxyacid shows efficient catalytic activity toward epoxidation of alkenes.

1. Introduction

Epoxidation of alkenes is a very useful reaction in industrial organic synthesis since the epoxides are key raw materials for the synthesis of fine chemicals and modern industrial process [1]. The most widely used method for epoxidation is the use of hydrogen peroxide as oxidant. Reactions with H_2O_2 generally require the presence of a catalyst [2]. In spite of considerable research efforts during the last decades, only a few useful catalytic systems for epoxidation with H_2O_2 have been developed. These include tungsten [3,4], manganese [5,6], and rhenium [7,8] based systems. An alternative is the epoxidation with peracids, which generally has some certain drawbacks, such as high price, risk of uncontrolled decomposition, and the formation of 1 equivalent of carboxylic acid as a byproduct [9]. These drawbacks might be overcome if a suitable catalyst is adopted into the reaction system. Consequently, the development of solid peroxyacid catalysts is expected to have a major impact in industrial applications as well as for scientific aspects. Supported organic peroxyacids are interesting alternatives for the oxygenation of organic substrates. Immobilization of peroxyacids on solid supports and their conversion to insoluble polymeric derivatives have been suggested as alternative ways of getting around the problems. Using these strategies, simplifies both the isolation of the reaction products and reagent recycling by suppressing neutralization and extraction operations for the separation of the carboxylic acid formed in the oxygen transfer step [10].

Silica is usually used as support due to its easy availability and low cost. However, the wide-range pore distribution, irregular pore shape, low pore volume and low specific surface area of silica often lead to low grafting amount of active sites, high mass-transfer resistance and poor catalytic activities [11]. To elevate the grafting amount, the preparation and application of mesoporous materials for such applications have become an intensively study in heterogeneous catalysis. SBA-15 has attracted a great deal of recent interest because of its tunable pore sizes (5–30 nm), well-organized array of straight channel, high surface area, open pore structure and narrow pore size distribution and shape selectivity, and also because of its thick pore walls, around 4 nm, which provide enhanced mechanical stability [12]. Unlike traditional inorganic materials, SBA-15 is typically synthesized under mild conditions, allowing for the incorporation of constituent building blocks with desired functionalities, leading to numerous functional SBA-15 that has shown promise for a number of applications, such as petroleum refining, medicinal applications, separations, catalysis, pollutant removal and sensors [13–17].

Considering these facts and taking into account all these, we decided to synthesis a novel supported peroxyacid catalyst on SBA-15, using polymerization of acrylic acid and then oxidation of carboxylic to peroxyacid groups. These multi-layered catalysts are synthesized by several steps including polymerization of acrylic acid and surface functionalization of SBA-15. The catalytic activity of the synthesized catalyst was investigated for the epoxidation of alkenes (Scheme 1).

2. Experimental

2.1. General

Tetraethylorthosilicate (TEOS), 3-chloropropyltrimethoxysilane (CPTMS) and Pluronic P123 triblock copolymer ($EO_{20}PO_{70}EO_{20}$, MW. 5800) were supplied by Aldrich. Other chemical materials were purchased from Fluka and Merck companies and used without further

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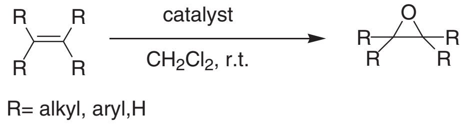


Scheme 1. Epoxidation of alkenes in the presence of SBA-polyperoxyacid.

purification. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel PolyGram SILG/UV 254 plates. The particle morphology was examined by SEM (Philips XL30 scanning electron microscope) and TEM (Zeiss — EM10C — 80 KV). Nitrogen adsorption measurements were conducted at 77.4 K on a Micromeritics ASAP-2020 sorptionmeter. The specific surface area and the pore size distribution were calculated by BET method and BJH model, respectively.

2.2. Synthesis of chloropropyl-grafted SBA-15 (SBA-Cl)

Chloropropyl-grafted SBA-15 (SBA-Cl) was prepared according to the reported method [19]. Pluronic 123 (4 g) was dissolved in 125 g of 2.0 M HCl solution at room temperature. After TEOS (8.41 g, 40.41 mmol) was added, the resultant solution was equilibrated at 40 °C for prehydrolysis, and then CPTMS (1.3 g, 6.5 mmol) was slowly added into the solution. The resulting mixture was stirred at 40 °C for 20 h and reacted at 95 °C under static condition for 24 h. The solid product was recovered by filtration and dried at room-temperature overnight. The template was removed from the as synthesized material by refluxing in 95% ethanol for 48 h (1.5 g of as-synthesized material per 400 mL of ethanol). Finally, the material was filtered, washed several times with water and ethanol, and dried at 50 °C.

2.3. Synthesis of SBA-Im-Allyl

To a solution of imidazole (0.476 g, 1 mmol) in 25 mL of dry toluene, sodium hydride (0.167 g, 7 mmol) was added and stirred under a nitrogen atmosphere at room temperature for 2 h to give sodium imidazole [20]. Then SBA-Cl (5.00 g) was added and the mixture was refluxed under a nitrogen atmosphere for 24 h. The resulting product was filtered and washed with ethanol (3 × 20 mL) and dried under vacuum at 100 °C for 8 h to give 3-(1-imidazole)propyl-SBA (SBA-Im). Then, 5.00 g SBA-Im was suspended in 5 mL of dry toluene and allyl chloride (0.535 g, 7 mmol) was added. The resulting mixture was stirred at 110 °C in an oil bath for 24 h, and then cooled to room temperature, filtered and washed with ether (3 × 20 mL) and dried under vacuum at 80 °C for 10 h.

2.4. Synthesis of SBA-polyacid

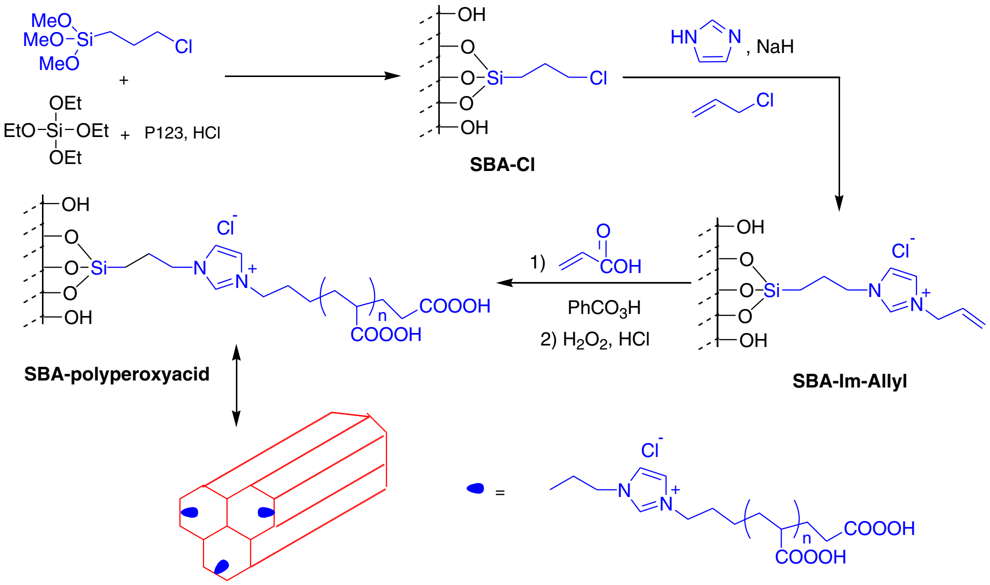
First, 2 g of SBA-Im-Allyl was suspended in 10 mL H_2O and 1.32 mmol (0.319 g) benzoylperoxide was added. The resulting mixture was stirred under a nitrogen atmosphere at 80 °C for 20 min. Then 30 mmol (2.16 g) of acrylic acid was added and the mixture was stirred at 80 °C for 20 h under nitrogen atmosphere. Finally, the resulting product was filtered and washed with water and methanol, and then dried at 60 °C.

2.5. Synthesis of SBA-polyperoxyacid

SBA-polyacid (2.5 g) was added in 9 mL of 70% H_2SO_4 and was stirred at 5 °C for 30 min. Then, 3.5 mL of 30% hydrogen peroxide was added at once and the mixture was stirred at 0–5 °C for 10 h. The solid was filtered and washed with cold doubly distilled water and dried at room temperature.

2.6. Procedure for epoxidation of alkenes catalyzed by SBA-polyperoxyacid

In a 25 mL round bottom flask, alkene (0.5 mmol) and catalyst (0.6–1 g) were added to 5 mL CH_2Cl_2 and completely mixed at room temperature for the lengths of time shown in Table 2. After completion of the reaction as indicated by TLC and GC, the heterogeneous reaction mixture was filtered and solid was thoroughly washed with dichloromethane in order to completely desorb any organic compound. The organic phase was treated with anhydrous magnesium sulfate, and evaporated in vacuum to give the products in 52–97% isolated yields. All the compounds were characterized on the basis of spectroscopic data (IR, ^1H & ^{13}C NMR) and by comparison with those reported in the literature.



Scheme 2. Synthesis of SBA-polyperoxyacid.

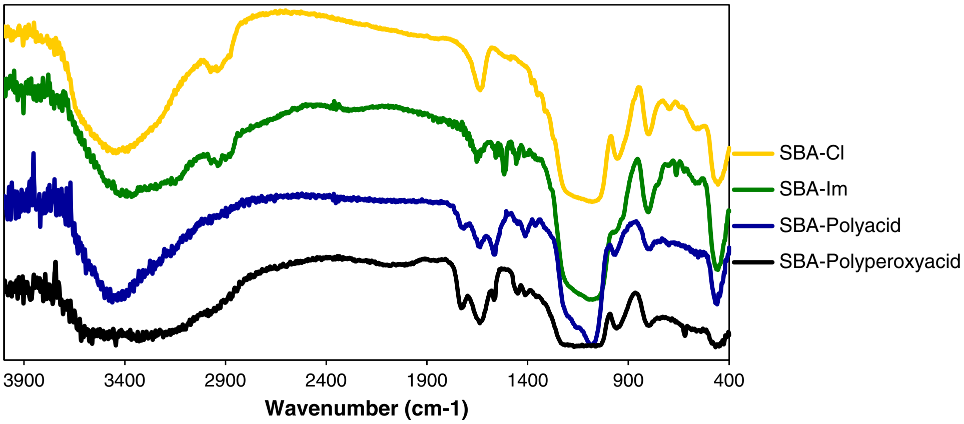


Fig. 1. FT-IR spectra of SBA-Cl, SBA-Im, SBA-polyacid and SBA-polyperoxyacid.

3. Results and discussions

First, SBA-propy-3-allyl-imidazolium chloride (SBA-Im-Allyl) was synthesized by nucleophilic substitution of SBA-propylchloride (SBA-Cl) with imidazole and then quaternization with allyl chloride according to the procedures given in Scheme 2. SBA-Im-Allyl containing terminal double bond was then used as support for immobilization of polyacrylic acid (SBA-polycarboxylic acid). Finally, the solid polyperoxyacid was obtained by treatment of the SBA-polycarboxylic acid with 30% hydrogen peroxide in an acid medium. Polyperoxyacid loading was calculated based on iodometric titration and shown the loading of 1.3 mmol of peracid per gram of hybrid material.

The FT-IR spectra of SBA-Cl, SBA-Im, SBA-polyacid and SBA-polyperoxyacid samples are shown in Fig. 1. In all materials the major peaks for SBA are around 1220, 1070, 801 and 473 cm^{-1} correspond to the typical Si–O–Si bands. Weak peaks associated with non-condensed Si–OH groups in the range of 940–960 cm^{-1} were also present. The strong peak and broad band around 1635 and 3500 cm^{-1} are due to the stretching vibration of SiO–H bond, the HO–H vibration of water molecule adsorbed on the silica surface and O–H vibration of carboxylic groups. The presence of peaks at 1200–1500 and 2870–3040 cm^{-1} in all cases was most probably due to the C–H bonds. The characteristic peaks of SBA-Im, SBA-polyacid and SBA-polyperoxyacid around 1568 cm^{-1} and 1644 cm^{-1} could be clearly observed which were attributed to $\mathrm{C{=}C}$, $\mathrm{C{=}N}$ stretching vibrations of the imidazole ring, respectively, and also a band around 1465 cm^{-1} is characteristic for the tertiary amine group. In the FT-IR spectrum of the SBA-polyperoxyacid, the observed peaks are approximately similar to that of SBA-polyacid.

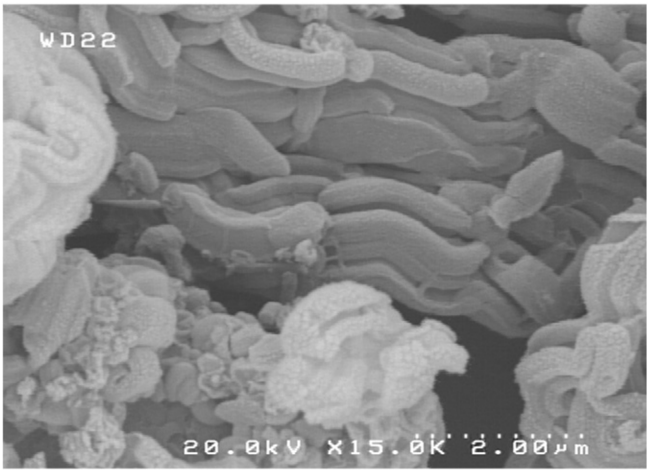


Fig. 2. The SEM image of SBA-polyperoxyacid.

Scanning electron microscopy (SEM) is a useful tool for determining the size distribution and particle shape. The morphological characterization and the particle size distribution of SBA-polyperoxyacid were performed by measuring SEM and TEM (Figs 2 and 3). Fig. 2 shows the SEM micrograph of the catalyst, which indicated long-range, three dimensional and mesoporous ordering. Fig. 3 depicts the TEM images of SBA-Cl and SBA-polyperoxyacid microspheres. From the TEM images, the pore structure and orderly pore arrangement could be clearly observed and confirmed the long-range, three dimensional and

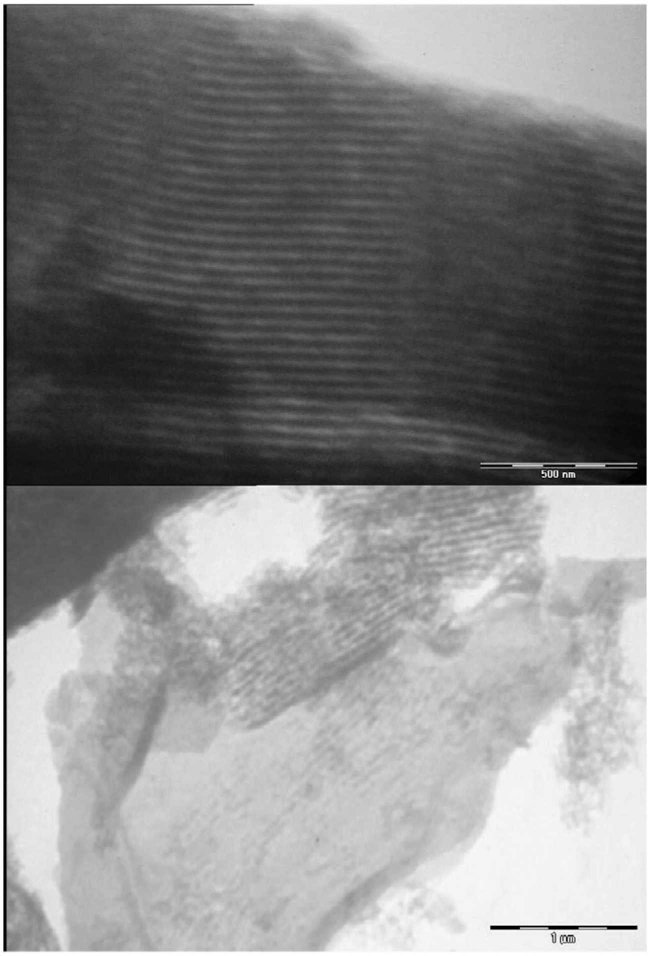


Fig. 3. The TEM images of SBA-Cl and SBA-polyperoxyacid.

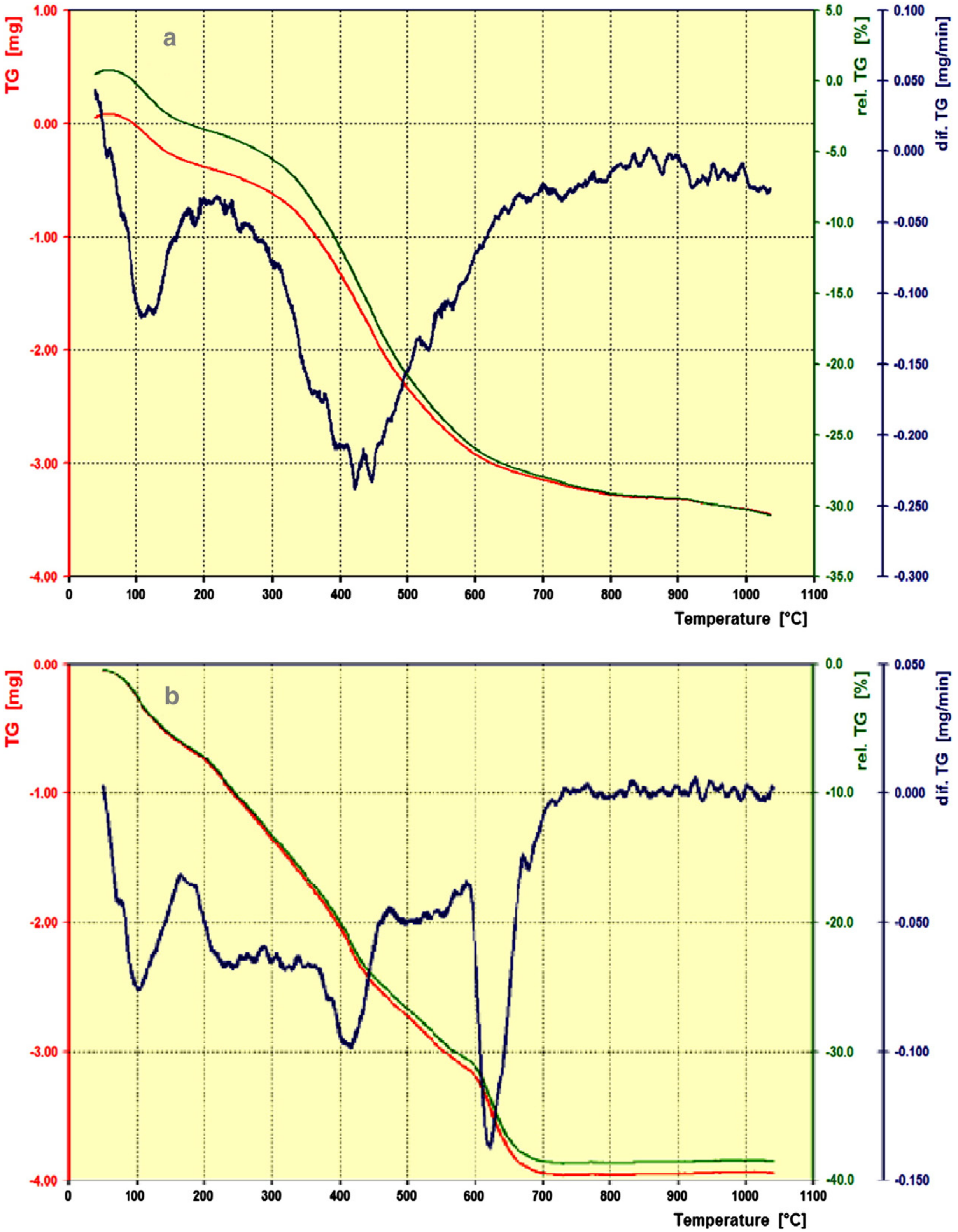


Fig. 4. TGA–DTG analysis of (a) SBA-Cl and (b) SBA-polyperoxyacid.

mesoporous ordering in this organocatalyst. TEM further confirmed that polymeric part covered the surface of silica support.

Fig. 4 showed the thermal gravimetric analysis–derivative thermogravimetric analysis (TGA–DTG) for SBA-Cl and SBA-polyperoxyacid. In both case the weight loss below 200 °C might be due to the loss of the adsorbed water as well as dehydration of the surface – OH groups. The thermal analysis further demonstrates that the polymerization of acrylic acid was successfully occurred on SBA structure. In the range of 300–600 °C, weight loss for SBA-Cl may be associated to the thermal decomposition of propyl group and for SBA-polyperoxyacid due to the

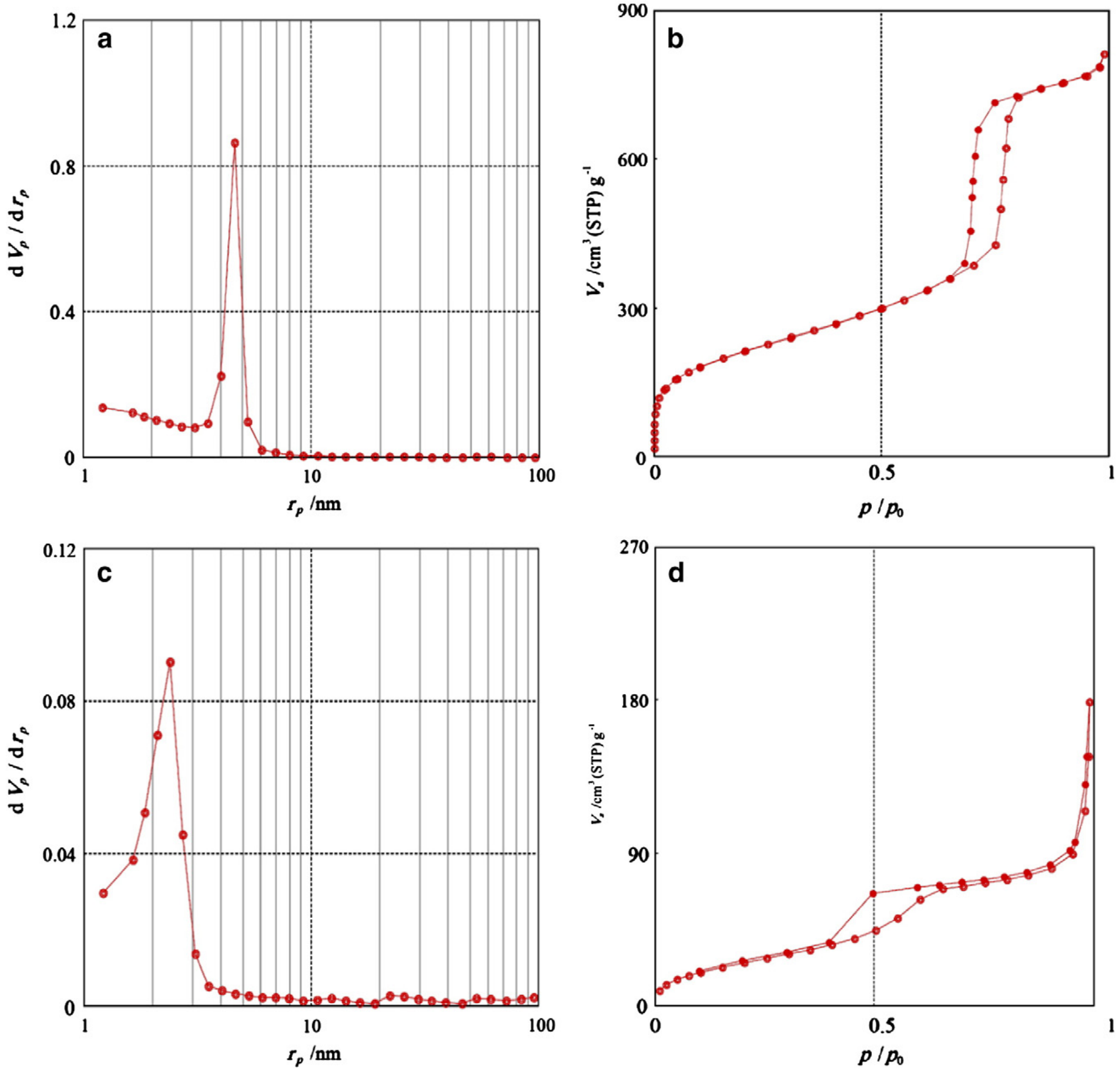


Fig. 5. Pore size distributions of SBA-Cl (a), SBA-polyperoxyacid (c) and nitrogen adsorption–desorption isotherms of SBA-Cl and (b), SBA-polyperoxyacid (d).

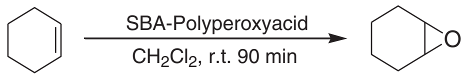
propyl and allyl imidazole group decomposition. In Fig. 4b, weight loss in the temperature range of 600–700 °C can be assigned to the decomposition of the polymeric part of the catalyst.

The nitrogen adsorption–desorption isotherms of SBA-Cl and SBA-polyperoxyacid are presented in Fig. 5. Both samples exhibited type IV isotherms, implying that the mesostructures are highly stable under acid/base treatment. This was further confirmed by the pore size distributions calculated by BJH method from the adsorption branches. It is well known that the introduction of homogenous catalysts or metals on porous supports shows a decrease in its specific surface area and pore volume [18]. The main structural characteristics determined experimentally are listed in Table 1. The BJH pore size distribution analysis shows that the material posses uniformly sized mesopores centered at ca. 97.2 Å for SBA-Cl and centered 47.6 Å for SBA-polyperoxyacid samples. The SBA-Cl exhibited a pore volume and surface area of 1.25 $cm^3\ g^{-1}$ and 753 $m^2\ g^{-1}$, respectively. After polymerization, the pore volume gets reduced to 0.26 $cm^3\ g^{-1}$ and surface area 98 $m^2\ g^{-1}$ for SBA-polyperoxyacid samples, due to the presence of peroxyacid part (Table 1).

Table 1
Specific surface area (S_{BET}), diameter pore and total pore volume.

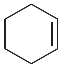
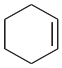
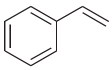
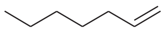
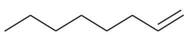
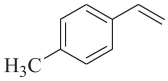
Sample	BET surface area ($m^2\ g^{-1}$)	Diameter (nm)	Pore volume ($cm^3\ g^{-1}$)
SBA-Cl	753	9.72	1.25
SBA-polyperoxyacid	98	4.76	0.26

To evaluate the catalytic activity of SBA-polyperoxyacid as heterogeneous catalyst in the epoxidation of alkenes, cyclohexene epoxidation was examined to determine whether the use of SBA-polyperoxyacid was efficient and to investigate the optimize conditions. Various



Scheme 3. Epoxidation of cyclohexene.

Table 2
Epoxidation of alkenes in the presence of SBA-polyperoxyacid in CH_2Cl_2 at room temperature.

Entry	Alkene	Molar ratio of catalyst/alkene	Time (h)	Yield (%)
1		1.5	1.5	76
2		2	1.5	97
3		2	4	52
4		2	3	83
5		2	4	66
6		2	3	98/74[a]

[a] Conversion.

conditions were screened to test the efficiency of the catalyst. Excellent yield of reaction was obtained under the optimized conditions using a catalyst/alkene molar ratio of 2, in CH_2Cl_2 as solvent at room temperature in 90 min (Scheme 3).

Subsequently, with optimal conditions in hand, the generality and synthetic scope of this protocol were demonstrated by epoxidation of other alkenes. Epoxidation of different alkenes was carried out by the use of SBA-polyperoxyacid in CH_2Cl_2 as solvent at room temperature (Table 2). The alkenes oxidation took place smoothly and easily to afford the corresponding epoxides as exclusive products according to TLC and GC. It is worthy to note that epoxides did not undergo significant ring-opening reactions catalyzed by the silica surface, and other compounds as the usual side products in oxidation of alkenes were not observed in this method.

The filtrated catalyst can be recycled by treatment with 30% hydrogen peroxide in acid medium. The reusability of the catalyst in the epoxidation of cyclohexene was evaluated. In this procedure, after completion of each reaction the catalyst was filtered. The recovered catalyst was treated with 30% hydrogen peroxide in acid medium and reused (Fig. 6). The results illustrated in Fig. 6 showed that the catalyst can be reused for up to four cycles without losing its activity.

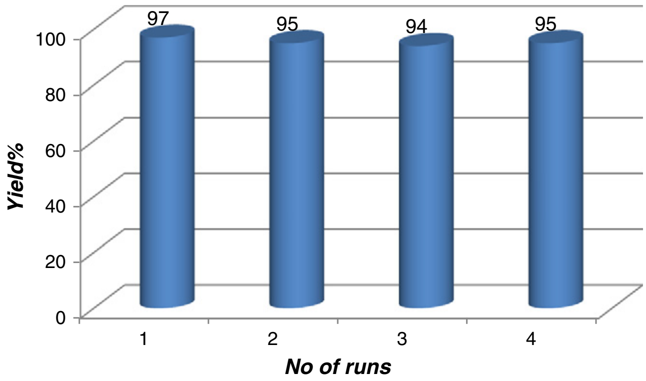


Fig. 6. Recyclability of catalyst.

4. Conclusion

In summary, we prepared a novel green heterogeneous polyperoxyacid catalyst by anchoring polyacrylic acid onto the surface of SBA-propy-3-allyl-imidazolium chloride. The properties of samples were characterized by FT-IR, SEM, TEM, TGA–DTG and BET analysis and the loading of the catalyst was measured by iodometric titration. The catalytic activity of the synthesized SBA-polyperoxyacid was successfully investigated for the epoxidation of alkenes. Solid catalyst can be easily recycled by a reaction with hydrogen peroxide solution in an acid medium. This method offers several advantages including high yield and clean reaction, short reaction time, ease of separation and recyclability of the solid catalyst.

Acknowledgments

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