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ORIGINAL PAPER

Synthesis and characterization of supramolecule grafted on modified magnetic nanoparticles: new hybrid organic–inorganic phase transfer catalyst

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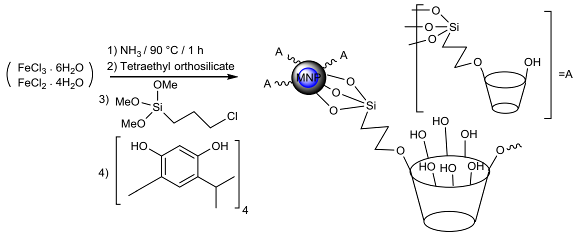
Abstract In this study, for the first time, calix[4]resorcinarene was grafted on the silica-coated magnetic nanoparticles (MNPs-Si) which efficiently catalyze one-pot epoxide ring opening reaction in excellent yields in a very short reaction time. Various advantages associated with this protocol include simple workup procedure, short reaction times, and high product yields. High catalytic activity and ease of recovery, using an external magnetic field, are additional eco-friendly attributes of this catalytic system.

Graphical abstract



Keywords Nanostructures · Magnetic properties · Heterogeneous catalysis · Nucleophilic additions · Phase-transfer catalysis · Supramolecular chemistry

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Introduction

Nanotechnology is a multidisciplinary branch of science which encompasses numerous applications in a variety of fields including electronics, optics, magnetism, energy technology, and chemistry [1–6]. The advent of nanoparticles has opened up a new era in many different fields of studies along with other nanomaterials and it should be noted that the field of catalyst has also been influenced. Organic/inorganic hybrid nanomaterials with controllable chemical compositions and structures, large surface-to-volume ratios, various surface properties, and functionalities can be regarded as fascinating nanotechnological objects with many optical, electrical, antibacterial, and catalytic properties [7, 8]. Among these, magnetic nanoparticles have emerged as a robust, high surface area heterogeneous catalyst support; they are good alternatives to filtration or centrifugation [9–13]. This strategy reduces the loss of catalyst and enhances reusability, rendering the catalyst cost-effective and promising for industrial applications.

As many studies have demonstrated the potential of supramolecular science, the *cis*-calix[4]resorcinarene have been interested by many chemists in recent years. These compounds are large cyclic tetramers with diverse application as macrocyclic receptors, such as dendrimers in biological systems, nanocapsules, nanoparticles, optical chemosensors, and supramolecular tectons as components in liquid crystals, molecular switches, selective membranes, HPLC stationary phase as ion channel mimics [14–17].

In addition, *cis*-calix[4]resorcinarenes possess a cup-like hydrophobic cavity surrounded by hydrophilic groups, and these properties allow them to be used as phase transfer catalyst. The possibility of modifying these structures either via the phenol hydroxyl groups or substitutions on the aromatic ring or even from the lower rim resulted in an increase in their potential to form multifunctional compounds.

In this context and in continuation of our previous studies [18–20], a heterogeneous catalyst has recently been developed based on calix[4]resorcinarene immobilized on silica-coated magnetic nanoparticles as an efficient phase-transfer catalyst in the synthesis of azidohydrins. Although a variety of new and mild procedures to effect this transformation have been reported, most of them have some limitations [21]. Therefore, in this report, a probable application is introduced and described for the synthesized nanomaterial which overcomes these limitations for the transformation of epoxides to β-azidohydrins as a new nanocatalyst (Scheme 1).

Results and discussion

Scheme 1 shows the schematic representation of the sequence synthetic pathway for MNPs-Si-resorcinarene catalyst. Magnetite nanoparticles were prepared with literature method [22]. These particles are easily prepared by adding a base to an aqueous mixture of Fe^{2+} and Fe^{3+} chloride then silica-coated magnetite (Fe_3O_4/SiO_2 core/shell) nanoparticles was synthesized. Moreover, the coating of MNPs-Si with resorcinarene can be easily accomplished using inexpensive and routine chemicals 3-chloropropyltriethoxysilane (CPTES) (Scheme 1). To confirm the coating of the magnetite surface through the silylation reaction and verify the formation of hybrid nanocomposite, FT-IR spectra of MNPs-Si-resorcinarene in the region of 400–4000 cm^{-1} (Fig. 1).

Scheme 1

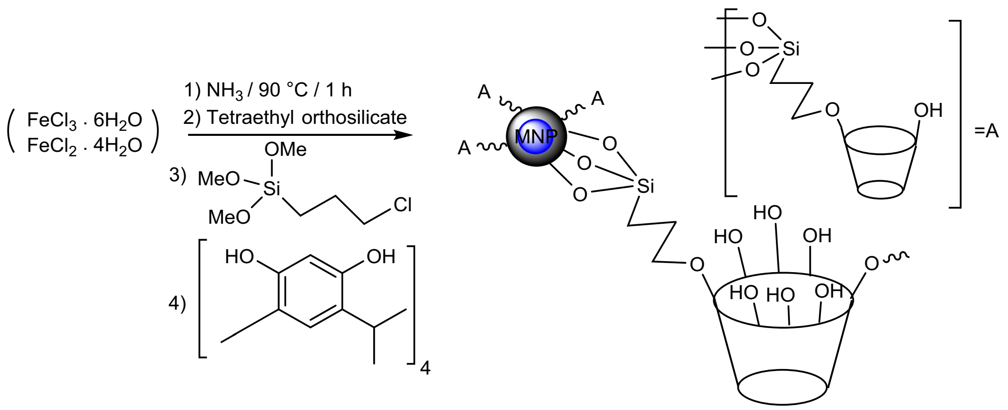
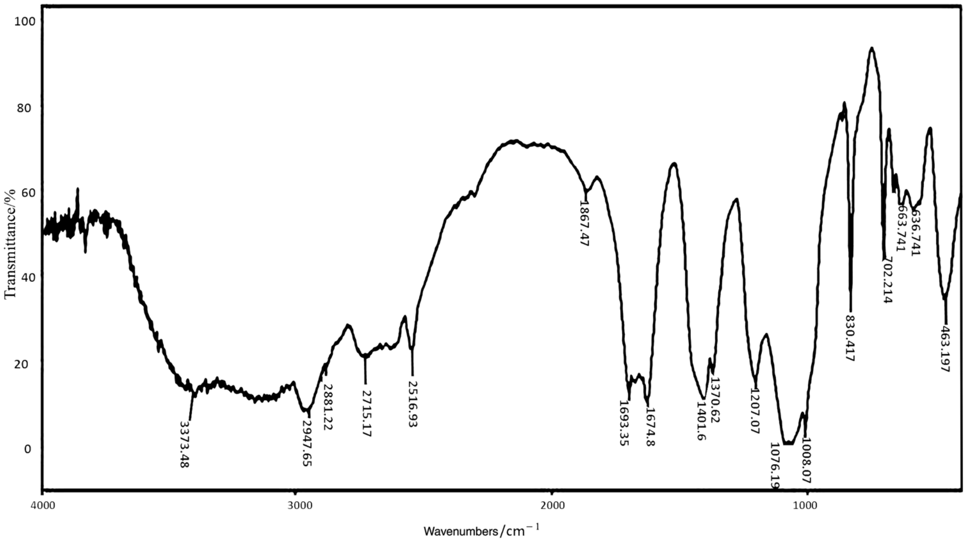


Fig. 1 FT-IR spectra of calix[4]resorcinarenes immobilized on modified magnetic nanoparticles



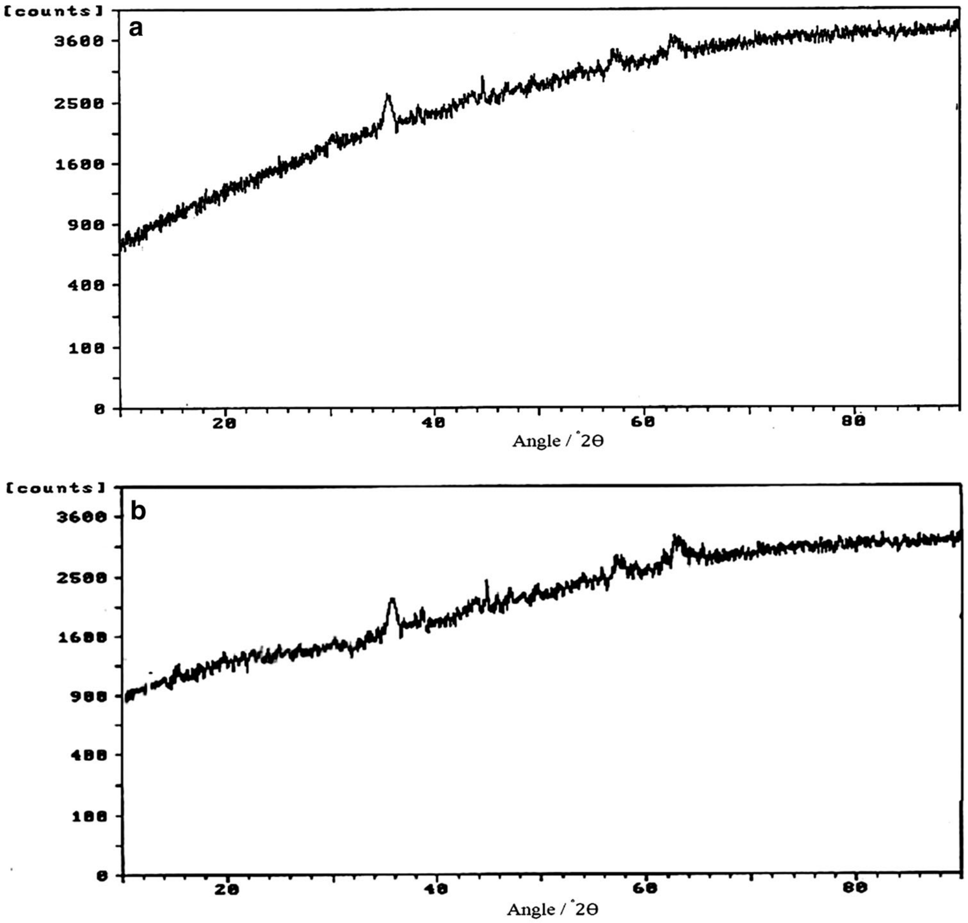


Fig. 2 XRD pattern of prepared calix[4]resorcinarenes immobilized on modified magnetic nanoparticles

The IR spectra of MNPs-Si-resorcinarene shows peak in the range of 3500–3200 cm^{-1} attributed to the hydroxyl stretching of internal phenol hydroxyl groups. The propyl groups attached to the resorcinarene framework in MNPs-Si-resorcinarene are identified by methylene stretching bands at 2959 and 2870 cm^{-1}. A strong peak near 1100 cm^{-1} is attributed to corresponding to the Si–O–Si stretch of linker and MNPs-Si. The peaks at 1604 and 1450 cm^{-1} were due to the C–C skeleton vibration of aromatic ring. Thus, FT-IR spectroscopy provides a good evidence for the formation of MNPs-Si-resorcinarene.

X-ray diffraction shows the large-angle XRD patterns of these samples in Fig. 2. The XRD pattern of Fe_3O_4 clearly showed some reflection peaks and confirmed the formation of a cubic spinel ferrite structure (JCPDS No. 19-0629) in Fig. 2a. The same reflection peaks appeared in the XRD patterns of the synthesized samples of MNPs-Si-resorcinarene in Fig. 2b, which suggested that the Fe_3O_4 crystallite phase was still maintained in the MNPs-Si-resorcinarene nanoparticles. The broad peaks indicate the higher degree of crystalline nature of the prepared material (Fig. 2a, b).

A typical scanning electron micrograph of the prepared MNPs-Si-resorcinarene is shown in Fig. 3. The SEM image shows the aggregation of the hollow MNPs-Si-resorcinarene spheres and also indicates that the obtained nanoparticles are composed of nearly uniform nanospheres with some agglomerations (Fig. 3).

The nanoparticle size and morphology of MNPs-Si-resorcinarene were investigated by TEM. Figure 4 shows the TEM image of the synthesized samples MNPs-Si-resorcinarene, although aggregated phenomenon of some nanoparticles was also observed, the particle diameters of the nanoparticles have spherical morphologies and monodispersed with less than 100 nm average diameter range, which is in agreement with the SEM observation. It indicated that the chemical modification of the Fe_3O_4 did not cause the significant increase of the particle size, and the advantages of magnetic nanoparticles can be maintained (Fig. 4).

To study the magnetic properties of magnetite nanoparticles before and after silica coating, silica particles, the hysteresis loops of magnetite nanoparticles and magnetic silica particles and also resorcinarene-linker groups at room temperature using vibrating-sample magnetometer were registered shown in Fig. 5a. The inset of Fig. 5 is the magnetization curve of magnetite nanoparticles, showing

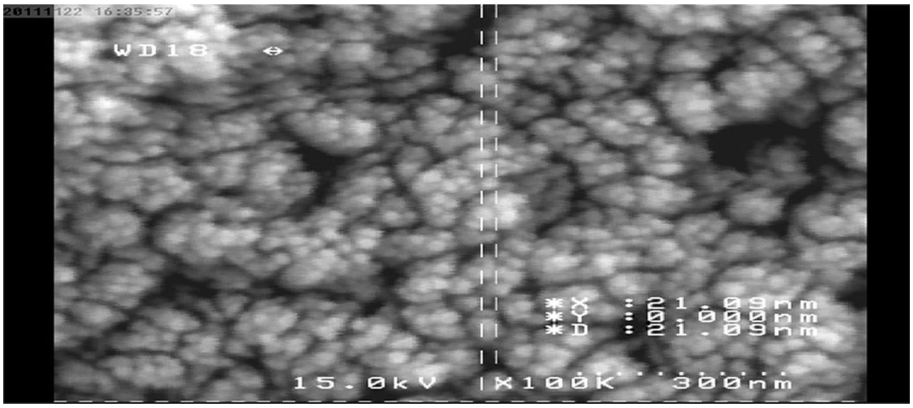


Fig. 3 SEM image of calix[4]resorcinarenes immobilized on modified magnetic nanoparticles

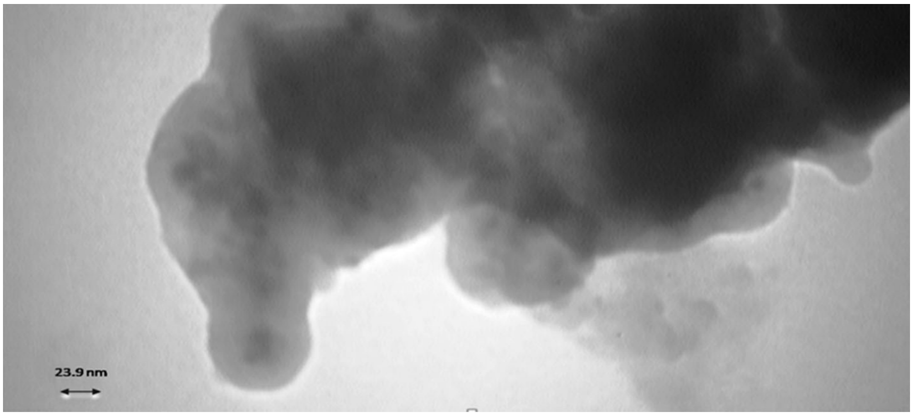


Fig. 4 TEM image of calix[4]resorcinarenes immobilized on modified magnetic nanoparticles

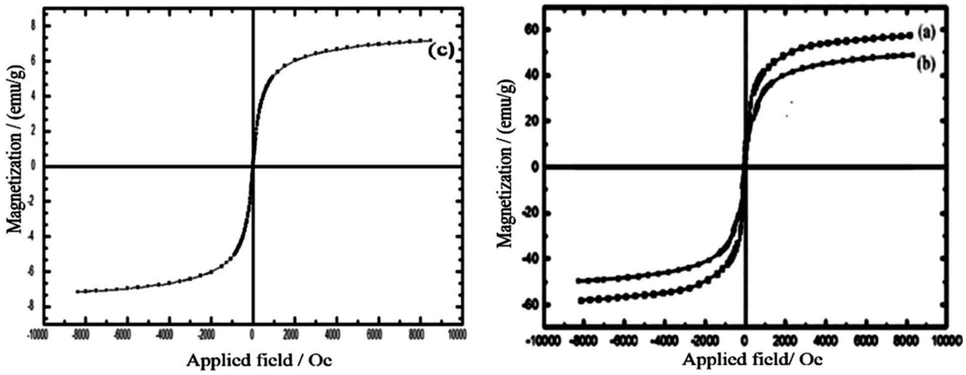


Fig. 5 VSM magnetization curve of **a** the Fe_3O_4 nanoparticles, **b** the silica coated Fe_3O_4 nanoparticles, and **c** calix[4]resorcinarenes immobilized on modified magnetic nanoparticles

magnetic property and saturation magnetization of about 60 emu/g of magnetite nanoparticle.

As it could be seen in Fig. 5b, c similar to magnetite nanoparticles, surface coating of the magnetite nanoparticles with silica and MNPs-Si-resorcinarene shows super paramagnetic behaviors, indicating that magnetite nanoparticles remained in the composite particles. Slight decrease of the saturation magnetization of the MNPs-Si-resorcinarene was due to the successful grafting of calix[4]resorcinarene on the surface of Fe_3O_4 nanoparticles (Fig. 5).

The thermal behavior of MNPs-Si-resorcinarene was investigated by TGA analysis. Figure 6 shows the TGA curve for the prepared MNPs-Si-resorcinarene. Four different slops can be observed from the TGA curve in Fig. 6 as a function of temperature. At first, the absorbed water was heated at 147 °C, due to the hydrophobic nature of the prepared nanocomposite material, the amount of adsorbed water was only 4 % wt. The second weight loss step of about 20 % started from the region of 195 °C was due to the cleavage of the linker grafted to resorcinarene, then the degradation at 375 °C, probably, is due to the thermal

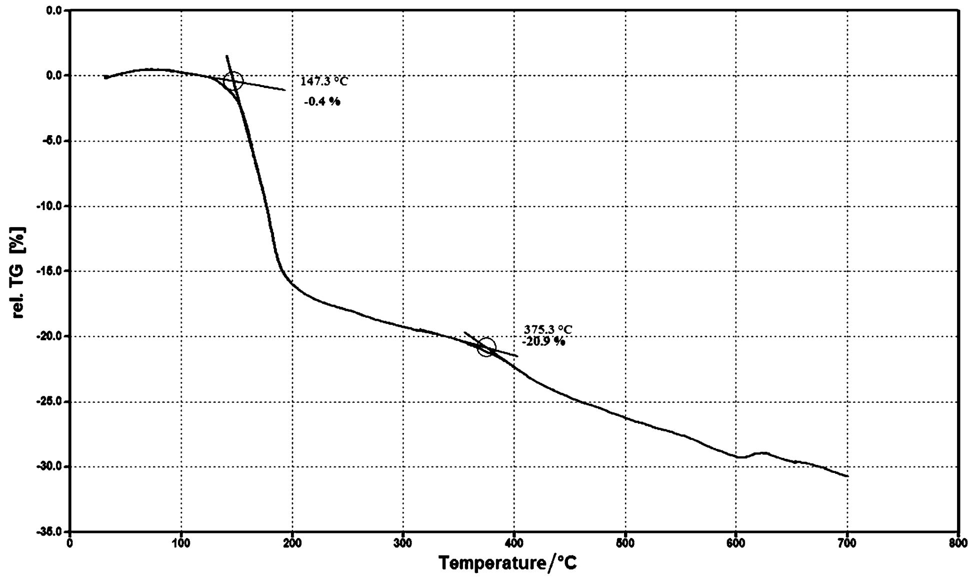


Fig. 6 TGA curve of prepared calix[4]resorcinarenes immobilized on modified magnetic nanoparticles

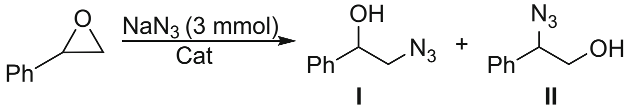
decomposition of resorcinarene units. When temperature is up to 600 °C, organics are completely denatured and only magnetic nanoparticles remain. Thus, the TGA curves also confirm the excellent chemical stability of this compound in high temperature (Fig. 6).

Epoxides are widely used in organic synthesis reactions of the fine chemicals and pharmaceutical industries [22]. The azidolysis of phenyl glycidyl ether (1 mmol), sodium azide as a test reaction was carried out to investigate the catalytic properties of the prepared MNPs-Si-resorcinarene (Scheme 2).

TLC analysis of the reaction mixture shows the completion of the reaction after 75 min and produced 1-azido-3-phenoxy-2-propanol in quantitative yield (Table 2, entry 1). To show the general applicability of the method and also ability of MNPs-Si-resorcinarene as nanomagnetic phase-transfer catalyst and molecular host system, the ring opening epoxide with this catalyst was applicable for a wide range of epoxides in Table 2.

Because of the predominant attack of azide ion on the less hindered carbon of the epoxide, all the terminal epoxides gave highly regioselective azidohydrins in quantitative yields. Due to formation of the stabilized benzylic cation during the reaction, ring opening of styrene oxide with NaN_3 resulted in 2-azido-2-phenylethanol as the major product with selectivity 80:20 (Table 2, entry 2).

Scheme 2



With cyclic epoxides, the ring opening completely took place via a trans-stereospecific pathway and giving only the *trans* isomers (Table 2, entry 6). This reaction was performed in short time with excellent yield. In case of acyclic terminal olefins (Table 1, entries 3–5), the major product results from the attack of nucleophile at the less substituted carbon to give 1,2-azidoalcohol in good to excellent yields.

The catalytic performances of this reusable catalyst were compared with some of the other literatures for the model reaction under optimized conditions (Table 1, entry 1). The results show a greater superiority of catalyst. It can be seen that the heterogeneous catalyst exhibited a significantly higher turnover number and turnover frequency than those reported for other catalytic systems (Table 1, entries 2-5).

The structure of all the products was settled from their analytical and spectral (IR, ^{1}H NMR) data and by direct comparison with authentic samples. Obviously, in the absence of MNPs-Si-resorcinarene or in the presence of the initial resorcinarene, the reaction was found to exhibit very negligible activity and even after prolonged reaction time a considerable amount of starting material was remained.

It is presumable that, the catalytic activity of MNPs-Si-resorcinarene as a phase transfer catalyst in ring opening epoxides reaction could be attributed to formation inclusion complex epoxide with hydrophobic porous of functionalize resorcinarene, and via hydrogen bonding of the epoxide oxygen to the outer OH of resorcinarene. In addition, bare azide anion transfer and react with immobilized epoxide. Therefore, the high selectivity and shorter reaction time could be explained by this method.

It is worthy to note that reusability of the catalyst was an important character and a performance criterion of any industrial process. In this method, the catalyst can be

Table 1 Comparison of the catalytic performance of catalyst with other literatures

Entry	Reactant	Catalyst	Solvent	Temp.	Time/min	Yield/%	References
1	NaN_3	Nanocatalyst	H_2O	80 °C	75	93	Present work
2	$TMSN_3$	β-cyclodextrine	H_2O	r.t	300	45	[23]
3	NaN_3	PEG-300	Solvent free	60 °C	60	90	[24]
4	NaN_3	MPTC	H_2O	Reflux	30	85	[25]
5	$TMSN_3$	$Er(OTf)_3$	Solvent free	r.t	400	86	[26]
6	NaN_3	$[pbmim](fecl_4)_2$	H_2O	Reflux	75	85	[27]

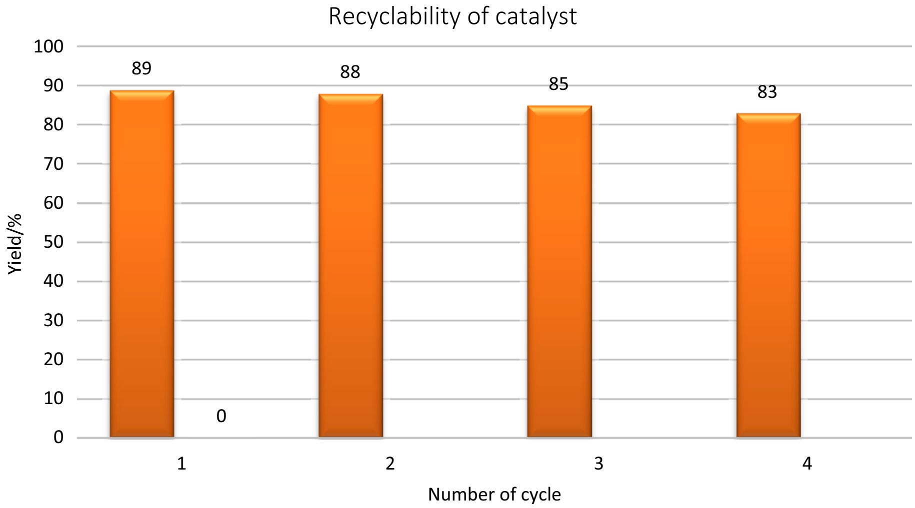


Fig. 7 Recyclability of catalyst

separated by simple magnetic decantation using a permanent magnet at the end of reaction, and reused after washing with ethanol and then drying in vacuum at 60 °C for 8 h. The nanocatalyst could be reactivated in a very easy way. No addition of acid, base, and special reagent, were needed during the reactivation. In every cycle, the nanocatalyst recovery was almost quantitative. After the third cycle, the yield was slightly decreased, indicating that the catalyst possessed an excellent reusability under the reaction conditions. The drop of product yield at the 4th catalytic cycle may be due to the clogging of some of effective nanoporous sites by reagents or even eluent (Fig. 7).

Conclusion

The novel design and synthesis of calix[4]resorcinarene was immobilized on modified magnetic nanoparticle. In addition, some characterizations and one of the probable application of this nanomaterial as a new magnetically recyclable and efficient nano-phase transfer catalyst was investigated. This catalyst exhibits several attractive features for the synthesis of fine chemicals. The magnetic core part is isolated and protected by the dense silica shell; thus, making its use under harsh reaction conditions possible. The high surface area of the mesoporous shell means that it can accommodate large amounts of the resorcinarene which can increase acidity, making the catalyst highly active. In addition, magnetic core can be readily utilized for the easy recovery and recycling of the catalyst with no significant loss of catalytic activity.

Experimental

Iron(II) chloride tetrahydrate (99 %), iron(III) chloride hexahydrate (98 %), epoxides, and other chemical materials were purchased from Fluka and Merck and used without further purification. The products were characterized by the comparison of their physical data, FT-IR and ^{1}H NMR and ^{13}C NMR spectra with known samples. NMR spectra were recorded in $CDCl_3$ on a Bruker Avance DPX 400 MHz spectrometer using TMS as internal standard. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates. The TGA curve was recorded on a BAHR, SPA 503 at heating rates of 10 °C

min^{-1}. The thermal behavior was studied by heating 1–3 mg of samples in aluminum-crimped pans under nitrogen gas flow, over the temperature range of 25–500 °C.

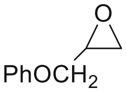
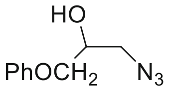
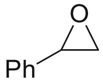
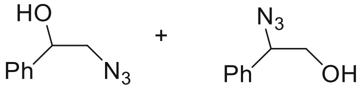
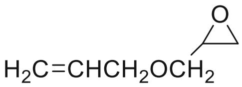
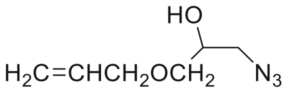
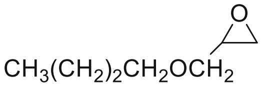
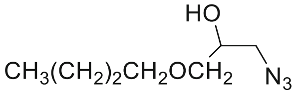
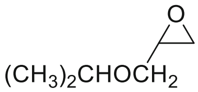
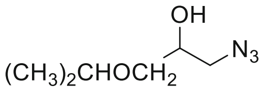
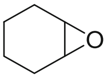
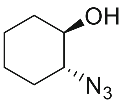
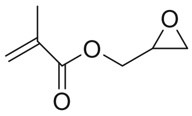
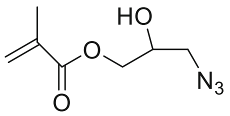
Preparation of magnetic nanoparticles grafted resorcinarene (MNPs-Si-resorcinarene)

MNPs-Si-resorcinarene involved some steps. First, magnetic nanoparticles (MNPs) were prepared via improved chemical coprecipitation method [28]. Silica coating of iron oxide nanoparticle was carried out using modified reported methods [29, 30], tetramethylcalix[4]resorcinarene was obtained by the condensation of resorcinol with acetaldehyde [30], dried at 70 °C for 6 h before using.

In the second step, for introducing of 3-chloropropyltriethoxysilane onto the surface of the magnetic nanoparticles, 0.4 g MNPs-Si powder was dispersed in 50 cm^3 of a mixture of ethanol and deionized water (1:1) by sonication and heated to reflux, then 1 mmol of the 3-chloropropyltriethoxysilane was added to the mixture. After mechanical agitation of mixture for 24 h, for immobilizing resorcinarene with 3-chloropropyltriethoxysilane grafted surface of MNPs-Si, 0.2 g of the calix[4]resorcinarene was added to a magnetically stirred mixture of 1.0 g 3-chloropropyltriethoxysilane grafted on MNPs-Si in 50 cm^3 toluene, 0.5 g potassium carbonate, and 0.02 g tetrabutylammonium bromide, and then heated to reflux and stir vigorously in nitrogen atmosphere for 24 h.

The mixture was then filtered, washed with 60 cm^3 ethanol then dried at room temperature to give the magnetic nanoparticles grafted on the upper rim of calix[4]resorcinarenes. The precipitation was separated by magnetic decantation and washed with ether several times. Product was dried in vacuum at 50 °C for 12 h.

Table 2 Reaction of various epoxides with sodium azide in the presence of the representative catalyst in water

Entry	Substrate	Product	Time /min	Yield /% [a]
1			75	93
2			30	89
3			35	85
4			20	83
5			15	87
6			25	82
7			20	84

Products were identified by comparison of their physical and spectral data with those of authentic samples

[a] Isolated yields

General procedure for ring opening of epoxides with NaN_3

MNPs-Si-resorcinarene (0.03 g) was added to a mixture of the epoxide (1.0 mmol) and NaN_3 (3 mmol) in 3 cm^3 water. The reaction mixture was magnetically stirred at 80 °C as much as the time shown in Table 2. After complete consumption of starting material as judged by TLC [using *n*-hexane:ethyl acetate (5:1) as eluent], the catalyst was concentrated on the sidewall of the reaction vessel using an external magnet, the aqueous phase was separated by decantation and extracted with diethyl ether (2 × 10 cm^3).

The extract was dried with calcium chloride ($CaCl_2$) and evaporated in vacuum to give corresponding product. For styrene oxide, further purification was achieved by preparative TLC or by silica gel column chromatography. The residual catalyst in the reaction vessel was washed and dried and then subjected to the next run directly.

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