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# An Fe₃O₄ nanoparticle-supported Mn (II)-azo Schiff complex acts as a heterogeneous catalyst in alcoholysis of epoxides

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A B S T R A C T

In this paper, an azo-containing Schiff base complex of manganese [$Mn^{2+}$-azo ligand-d@APTES-SiO₂@Fe₃O₄] immobilized on chemically modified Fe₃O₄ nanoparticles has been used as a magnetically retrievable catalyst for the alcoholysis of different epoxides to their corresponding alkoxy alcohols with methanol, ethanol and *n*-propanol. The newly magnetic nanoparticles (MNPs) were characterized by Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and vibrating sample magnetometry (VSM).

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## 1. Introduction

The recovery of expensive catalysts after catalytic reactions and reusing them without loss of their chemical activity are important factors for sustainable process management [1,2]. The difficulty in separating homogeneous catalysts from the reaction medium restricts catalyst recycling in industries, particularly in drug and pharmaceutical industries, owing to the issue of metal contamination in the cases of metal-catalyzed synthesis [3]. Surface functionalization of magnetic nanoparticles is a well-designed method to bridge the gap between heterogeneous and homogeneous catalysis [4]. Since such catalysts work under quasi-homogeneous conditions, their performance typically exhibits high selectivity, activity, and stability. In many cases, catalysts can be easily separated by magnetic decantation and reused [5,6].

The ring opening of epoxides' reactions with different nucleophiles are important reactions in organic synthesis because the 1,2-disubstituted products are often useful and valuable intermediates. A literature survey indicated that a variety of catalytic methods under either basic or acidic conditions have been developed using the ring opening of epoxides with alcohols that leads to β-alkoxy alcohols. However, many catalytic systems have significant drawbacks, such as tedious work-up procedures or hazardous chemical waste products, which prompted organic researchers to develop a simple, environmentally benign method [7–11].

As a part of our ongoing investigations into sustainable synthetic methods [12–16], we recently introduced new magnetically recoverable nanocatalyst systems for organic reactions [17,18]. In this study, we report on a synthesis approach, structural characterization, and catalytic ability of a novel nanoparticle supported azo Schiff base.

Schiff bases are present as reactants in many synthetic organic processes, as important scaffolds in organometallic chemistry, as backbones of precious catalysts and as pharmaceutical presidiums against a series of different diseases and pathological states [19].

## 2. Experimental

### 2.1. General

All chemicals were purchased from Merck, Aldrich and Fluka and used without further purification. TLC was performed on aluminum-backed silica gel 60 F₂₅₄ plates

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(0.2 mm thickness, Merck). Atomic absorption measurements were carried out on a Shimadzu AA-6300 spectrometer with a deuterium lamp background corrector. SEM-EDAX analyses were carried out using a Philips XL30 instrument. The TEM image was recorded using a Zeiss-EM10C-100 KV. Magnetism analysis was performed on a vibrating sample magnetometer (4 inch, Daghigh Meghnatis Kashan Company, Kashan, Iran) at room temperature. The FT-IR spectra were recorded using a BOMEM MB-Series 1998 FT-IR spectrometer.

### 2.2. Preparation of $Mn^{2+}$-azo ligand@Am-$SiO_2$@$Fe_3O_4$

First, 2 g of $SiO_2$@$Fe_3O_4$ was dispersed in 10 mL of dry toluene and, sonicated for 15 min using an ultrasonic bath. Then, 2 mL of (3-aminopropyl) triethoxysilane was added. The mixture was stirred and refluxed for 72 h under a nitrogen atmosphere. The particles obtained were filtered off, washed with ethanol and diethyl ether and dried under reduced pressure to obtain Am-$SiO_2$@$Fe_3O_4$.

Next, using the procedure described by Uruş et al. with a minor modification [20], 1 g of Am-$SiO_2$@$Fe_3O_4$ was added to a solution of 0.121 g, 1 mmol of (Z)-5-({2,4-dichloro-6-hydroxyphenyl}diazenyl)-2-hydroxybenzaldehyde in 10 mL of ethanol. The mixture was stirred under reflux conditions for 12 h. The resultant MNPs were removed by using an external magnet and washed several times with ethanol and dried well to generate Azo ligand@Am-$SiO_2$@$Fe_3O_4$.

Finally, to synthesis $Mn^{2+}$-azo ligand@Am-$SiO_2$@$Fe_3O_4$ nanoparticles, a mixture of 2.0 g Azo ligand@Am-$SiO_2$@-$Fe_3O_4$ in 10 mL of ethanol was sonicated for 15 min. Then, 0.173 g, 1 mmol of manganese acetate was added, and the resulting mixture was refluxed for 24 h. After removing the particles magnetically, the nanocomposites were washed with water and dried under reduced pressure.

### 2.3. Alcoholysis procedure

A mixture of epoxide (1 mmol), alcohol (5 mL) and $Mn^{2+}$-azo ligand@Am-$SiO_2$@$Fe_3O_4$ (0.05 g) was heated under reflux conditions for an appropriate time. After completion of the reaction monitored by GC or TLC analysis, the reaction mixture was cooled to room temperature and the magnetic nanocatalyst was separated by using an external magnet and washed with acetone for recycling experiments.

## 3. Results and discussion

The synthetic method employed to graft the azo Schiff ligand onto the silica-coated $Fe_3O_4$ and chelating ligands via nitrogen and oxygen atoms to the manganese center is outlined in Scheme 1. The first stage began with amination of the $SiO_2$@$Fe_3O_4$ surface using 3-(azidopropyltrimethoxy) silane (APTES) in toluene under reflux conditions. Am-$SiO_2$@$Fe_3O_4$ nanoparticles were subjected to a reaction with ethanol solution of the azo compound [(Z)-5-({2,4-dichloro-6-hydroxyphenyl}diazenyl)-2-hydroxybenzaldehyde]. The azo Schiff base was synthesized according to the reported procedure [21]. The ligand performed two roles: forming a complex with Mn(II) and enhancing the lipophilicity of the catalyst. Treatment of the latter nanoparticles with Mn(OAc) in ethanol under reflux conditions led to the target nanocomposites.

The structure analysis of the resultant $Mn^{2+}$-azo ligand@Am-$SiO_2$@$Fe_3O_4$ magnetic nanoparticles was then accomplished using FT-IR, SEM, EDX and VSM techniques (see Fig. 1).

The FT-IR spectrum showed several peaks corresponding to the $Fe_3O_4$ core, $SiO_2$ shell and azo Schiff ligand. The peak at ~580 $cm^{-1}$ was due to Fe–O vibration, and a broad peak at ~3423 $cm^{-1}$ was attributed to the Si–OH group. Also, a strong peak at ~1098 $cm^{-1}$ belonged to antisymmetric stretching vibrations of the Si–O–Si bond. The peaks at ~3100–2850 $cm^{-1}$, ~1622 $cm^{-1}$ and ~1480 $cm^{-1}$ corresponded to vibration of the C–H (aromatic rings and linker moiety), C=C, and N=N bonds, respectively.

The SEM and TEM images displayed a nearly spherical morphology and the nanosize of the $Mn^{2+}$-azo ligand@Am-$SiO_2$@$Fe_3O_4$ particles (Fig. 2).
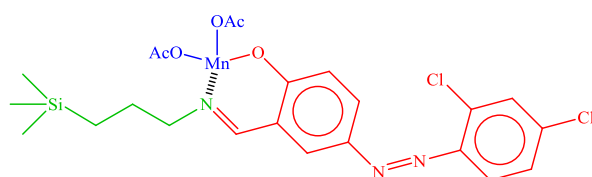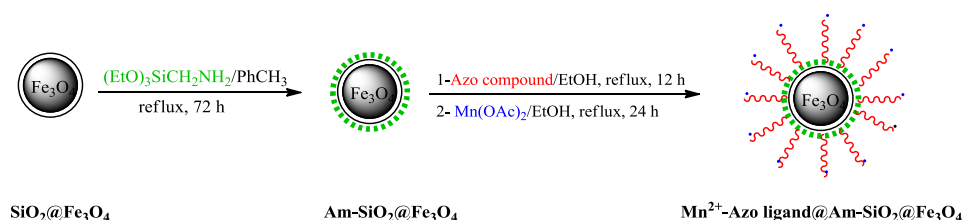


**Scheme 1.** Preparation of $Mn^{2+}$-azo ligand@Am-$SiO_2$@$Fe_3O_4$ nanoparticles.
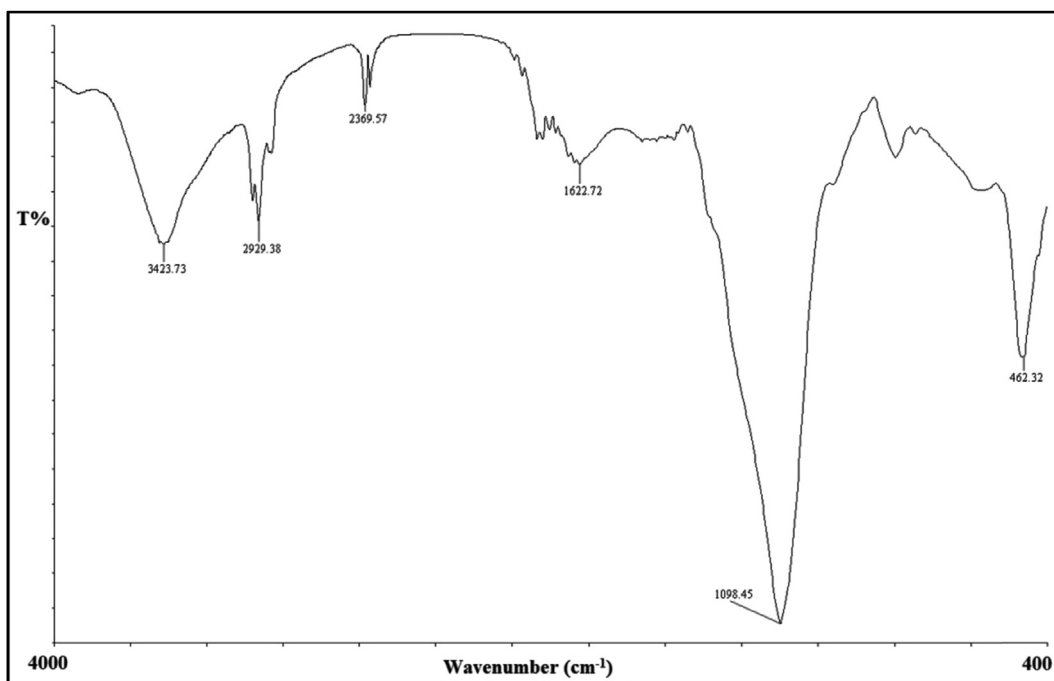
**Fig. 1.** The FT-IR spectrum of $Mn^{2+}$-azo ligand@APTES-$SiO_2$@$Fe_3O_4$.

The EDX imaging of the Mn (II)-azo Schiff complex grafted to $Fe_3O_4$ confirmed the presence of oxygen (33.2% wt), carbon (23.0% wt), silicon (19.7% wt), iron (12.6% wt), nitrogen (7.0% wt), chlorine (2.5% wt) and manganese (1.9% wt) (Fig. 3). The molar ratio of Mn/Cl is 0.5, which is compatible with the proposed structure.

The magnetic properties of $Mn^{2+}$-azo ligand@Am-$SiO_2$@$Fe_3O_4$ were also investigated at room temperature using a vibrating sample magnetometer (Fig. 4). Comparing the results of the neat $Fe_3O_4$ with $Mn^{2+}$-azo ligand@Am-$SiO_2$@$Fe_3O_4$, the saturation magnetization value decreases from 60 emu/g to about 15 emu/g. This decrease was due to the coating of the magnetite particles with non-magnetic materials: the $SiO_2$ shell, linker moiety and azo Schiff base ligands. However, the catalyst could still be simply separated from the solution by applying an external

magnetic force, though the saturation magnetization had been decreased (Fig. 5). The catalytic activity of the Mn loaded nanoparticles was investigated for the ring opening of epoxides with alcohols. First, treatment of 1 mmol of 2-(phenoxymethyl)oxirane with 5 mL of methanol, as a substrate and solvent, was chosen as a test reaction. The optimal reaction conditions were found to occur with 0.05 g of the magnetic nanocatalyst heated during the solvent refluxing. In addition, we did not detect conversion of the substrate in the absence of the catalyst or free Mn loaded nanoparticles (Azo ligand@Am-$SiO_2$@$Fe_3O_4$). Accordingly, a range of epoxides was subjected to a reaction with methanol, ethanol and $n$-propanol in the presence of $Mn^{2+}$-azo ligand@Am-$SiO_2$@$Fe_3O_4$. For all cases, Table 1 reveals that a complete conversion of only one isomer was obtained which is the regiochemical outcome attack
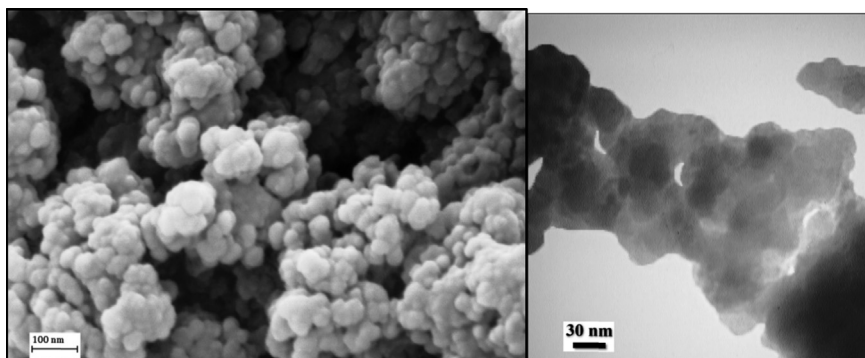


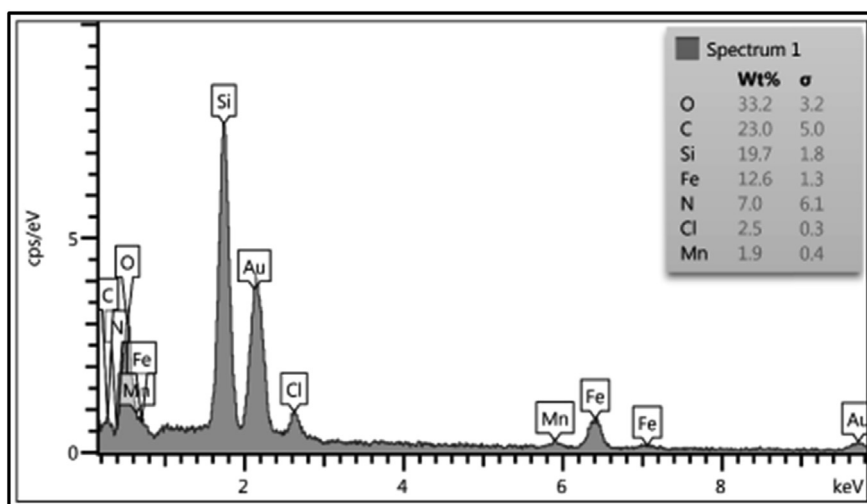**Fig. 2.** SEM (left) and TEM (right) images of the nanoparticles.

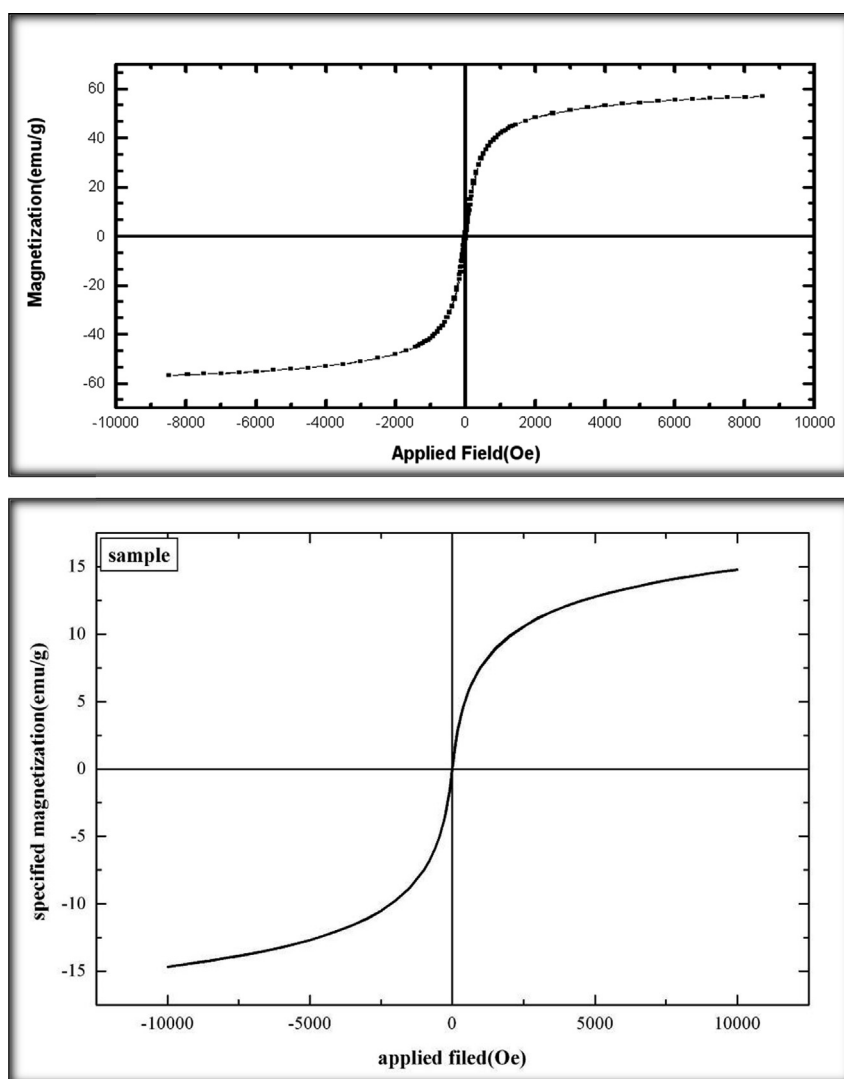**Fig. 3.** The energy-dispersive X-ray spectroscopy (EDX) of $Mn^{2+}$-azo ligand@APTES-$SiO_2$@$Fe_3O_4$.



**Fig. 4.** Room-temperature magnetization curves of $Fe_3O_4$ (upper) and $Mn^{2+}$-azo ligand@APTES-$SiO_2$@$Fe_3O_4$ (lower).
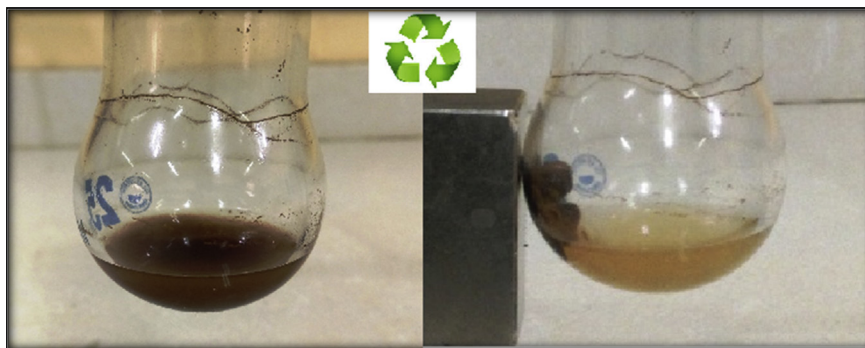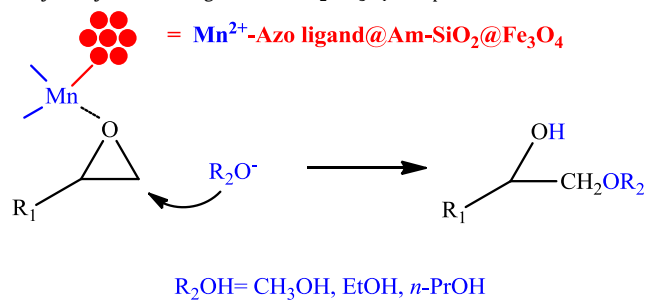
**Fig. 5.** Removing the catalyst from the reaction mixture by magnetic separation.
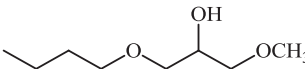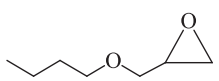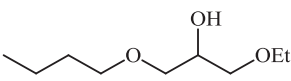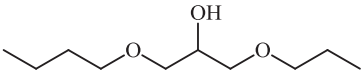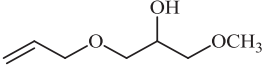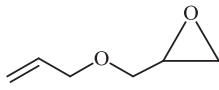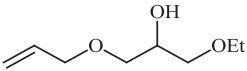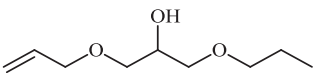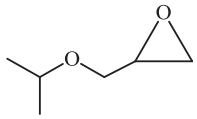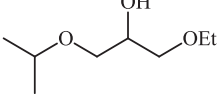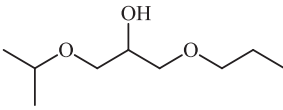
**Table 1**
Ring opening reaction with alcohols catalyzed by $Mn^{2+}$-azo ligand@Am-SiO$_2$@Fe$_3$O$_4$ nanoparticles.



$R_2OH= CH_3OH, EtOH, n\text{-PrOH}$

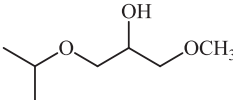| Entry | Epoxide | Alcohol | Product (s) | Time (h) | Conv.(%)[a] |
|---|---|---|---|---|---|
| 1 | | $CH_3OH$ | | 6 | 60/40 |
| 2 | Ph epoxide | EtOH | | 9 | 100 |
| 3 | | n-Propanol | | 7 | 75/25 |
| 4 | | $CH_3OH$ | | 2.5 | 100 |
| 5 | PhO epoxide | EtOH | | 3 | 100 |
| 6 | | n-Propanol | | 2 | 100 |

**Table 1** (*continued* )

| Entry | Epoxide | Alcohol | Product (s) | Time (h) | Conv.(%)[a] |
|-------|---------|---------|-------------|----------|-------------|
| 7 | | CH$_3$OH | | 2 | 100 |
| 8 | | EtOH | | 3 | 100 |
| 9 | | *n*-Propanol | | 2 | 100 |
| 10 | | CH$_3$OH | | 4 | 100 |
| 11 | | EtOH | | 2 | 100 |
| 12 | | *n*-Propanol | | 2.5 | 100 |
| 13 | | CH$_3$OH | | 2.5 | 100 |
| 14 | | EtOH | | 3 | 100 |
| 15 | | *n*-Propanol | | 1.5 | 100 |

[a] Determined by GC.

on the less substituted carbon of the aliphatic epoxides, with the exception of styrene epoxide. In this aryl epoxide, the major isomer resulted from an attack on the benzylic position (entries 1 and 3). To clarify the efficiency of the catalyst, the turnover number (TON) and turn over frequency (TOF) were calculated using the 0.34 mmol/g Mn obtained by EDAX, which are 58.8 and 6.5–39.2 h$^{-1}$, respectively.

The development of recoverable and recyclable catalysts represents a fascinating challenge for the industry [22]. Interestingly, the nanomagnetic catalyst could be reused at least five times without loss of activity in the synthesis reaction of 1-methoxy-3-phenoxypropan-2-ol (Fig. 6, conversion decreases from 100% to 92%).

When using a supported catalyst, a crucial issue is the possibility that some of the active sites could migrate from the solid support to the liquid phase, where these leached species could become responsible for a significant portion of the catalytic activity [23]. In order to investigate this issue, a mixture of the catalyst (0.5 g) and methanol was refluxed for 12 h. Then the nanoparticles were carefully separated by using an external magnet. A sample of the solution was then analyzed by an atomic absorption technique, and less than 1 ppm of Mn was detected.
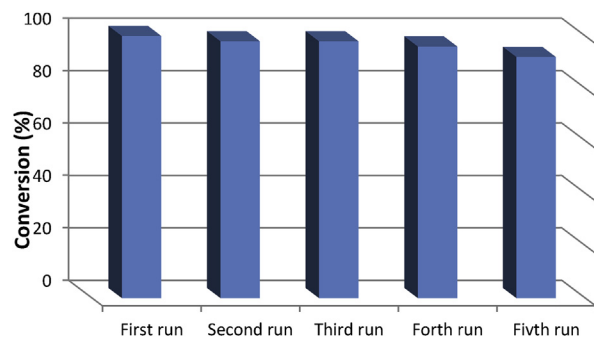
**Fig. 6.** Recycling of the nanocatalyst.

## 4. Conclusion

In summary, a new magnetite-supported organocatalyst [$Mn^{2+}$-azo ligand@APTES-$SiO_2$@$Fe_3O_4$] was successfully prepared, characterized and applied for the synthesis of β-alkoxy alcohols using the ring opening of epoxides with alcohols. The catalyst showed a good performance and high turnover frequency. Moreover, the catalyst can be easily retrieved from the reaction mixture and reused without any significant loss in catalytic activity.

## Acknowledgements

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