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Chemistry

THE IMMOBILIZED Cu-Ni-Fe-Cr LAYERED DOUBLE HYDROXIDE ON SILICA-LAYERED MAGNETITE AS A REUSABLE MESOPOROUS CATALYST FOR CONVENIENT CONVERSION OF EPOXIDES TO 1,2-DIACETATES

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Abstract. In this study, Cu-Ni-Fe-Cr layered double hydroxide (LDH) immobilized on silica layered magnetite (Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH) was investigated towards ring opening of diverse epoxides with acetic anhydride to afford vic-diacetates within 15–40 min in high yields. Reusability of the nano-LDH was also studied for 6 consecutive cycles without the significant loss of catalytic activity.

Keywords: Ac_2O, 1,2-diacetate, epoxide, Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH, ring-opening.

1. Introduction

Nowadays, heterogeneous catalysts are widely utilized in many organic transformations.[1-7] In this context, hydrotalcites (HTs) as a class of anionic and basic clay minerals and known as layered double hydroxides (LDHs) represent a high level of activity. They are frequently used as eco-friendly materials in the fields of catalysis,[8] anion exchange,[9] adsorption,[10] drug carriers,[11] and precursors of magnetic materials.[12] Although, layered double hydroxide systems are naturally existing, however, they can be also synthesized by the routine procedures. The chemical synthesis of hydrotalcites produces hydrotalcite materials possessing the aggregated particles with unacceptable size and morphology. In order to overcome this shortcoming, the combination of magnetic nanoparticles (MNPs) with LDHs gives the new nanostructured composite systems. Because of huge surface area to volume ratio and magnetic property, they exhibit the intensive selectivity and catalytic activity as well as easy separation capability from the reaction medium.[13-19]

On another hand, epoxides as one of the important building blocks and synthetic intermediates have attracted the attention of chemists to carry out various transformations.[20,21] They can react with different nucleophiles to afford 1,2-difunctional products. In this area, the nucleophilic ring-opening of epoxide with acetic anhydride produces 1,2-diacetates (*vic*-diacetates) in a direct approach. Literature review shows that various catalyst or reagent systems have been reported for the titled transformation.[22-35] Although most of the reported procedures are useful and convenient, however, they generally suffer from using expensive organic solvents and reagents, strongly basic/acidic reaction conditions, long reaction times, undesirable yields, and limitation to use structurally different epoxides. Therefore, the development and introduction of green synthetic methods which utilize the efficient recoverable catalyst systems is still a subject of interest.

In line with the outlined strategies and continuation of our research program on synthesis and application of magnetic layered double hydroxide system,[36] herein, we wish to introduce the fabrication and characterization of the immobilized Cu-Ni-Fe-Cr layered double hydroxide on silica-layered magnetite, Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH, as a novel and mesoporous material. Next, catalytic activity of the prepared nanocomposite system was investigated towards direct transformation of epoxides to the corresponding 1,2-diacetates in the absence of any solvent and under oil bath (353 K) conditions (Fig. 1).

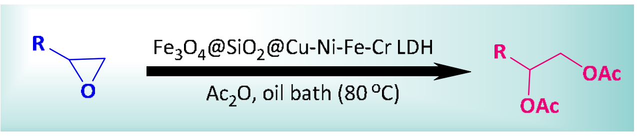

Fig. 1. Ring-opening of epoxides with Ac_2O catalyzed by Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH system

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2. Experimental

2.1. Materials and Methods

All materials and reagents were purchased from commercial sources and used without further purifications. FT-IR, ^1H NMR spectra were recorded on Thermo Nicolet Nexus 670 and Bruker Avance 300 MHz spectrometers, respectively. The obtained products were characterized using physical and spectral data followed by a comparison with the reported data in literature. Purity of chemicals as well as progress of the reactions was monitored by TLC over silica gel 60 F_{254} aluminum sheet. X-ray diffractions were recorded by X'PertPro Panalytical diffractometer at 40 kV (30 mA, CuKα radiation source, $\lambda = 1.5418$ Å) in $2\theta = 10°–80°$. Size and morphology of the particles were determined using SEM images by FESEM ZEISS-Sigma VP instrument. Transmission-electron microscopy images (TEM) were captured using Zeiss-EM10C instrument in an accelerating voltage of 100 kV. Magnetic property of the nanocatalyst was measured by vibrating sample magnetometer (Meghnatis Daghigh, Iran) under magnetic fields up to 20 KOe. The irradiation of ultrasound was carried out on SOLTEC SONICA 2400MH S3 (305 W).

2.2. Preparation of Fe_3O_4

Magnetically nanoparticles of Fe_3O_4 were prepared through a chemical co-precipitation of chloride salts of Fe^{3+} and Fe^{2+}.[37] Generally, a solution of $FeCl_3{\cdot}6H_2O$ (5.838 g, 0.0216 mol) and $FeCl_2{\cdot}4H_2O$ (2.147 g, 0.0108 mol) in a round-bottom flask containing distilled water (100 mL) was prepared and then stirred for 10 min at 358 K under N_2 atmosphere. After that, by adding an aqueous solution of ammonia (10 mL, 25 wt. %), deep brown nanoparticles of Fe_3O_4 were immediately precipitated. The mixture was continued to stir at 358 K for 30 min under N_2 atmosphere. After cooling to the room temperature, nanoparticles of Fe_3O_4 were separated by an external magnetic field and washed with a solution of NaCl (0.02M) and distilled water.

2.3. Preparation of Silica-Layered Magnetite

Layering of silica on nanoparticles of Fe_3O_4 was carried out *via* the reported procedure.[38] Magnetically nanoparticles of Fe_3O_4 (1.5 g) were dispersed in distilled water (20 mL) by sonication for 15 min. 2-Propanol (200 mL) was then added and the resulting suspension was sonicated for 30 min. Subsequently, PEG-400 (5.36 g), distilled water (20 mL), NH_4OH (25 %, 10 mL), and tetraethyl orthosilicate (TEOS, 2 mL) were respectively added and the mixture was stirred for 28 h at room temperature. The resulting nanoparticles of silica layered magnetite, Fe_3O_4@SiO_2, were magnetically separated and washed with distilled water and ethanol to allow for drying under air atmosphere.

2.4. Preparation of Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH

Immobilization of Cu-Ni-Fe-Cr layered double hydroxide moiety on Fe_3O_4@SiO_2 nanoparticles was carried out *via in situ* growth procedure. In an Erlenmeyer flask, a suspension of Na_2CO_3 (0.01 mol, 1.060 g), NaOH (0.004 mol, 0.160 g), and Fe_3O_4@SiO_2 (0.25 g) in distilled water (30 mL) was prepared. In another flask, a solution of $FeCl_3{\cdot}6H_2O$ (0.003 mol, 0.811 g), $Cr(NO_3)_3{\cdot}9H_2O$ (0.002 mol, 0.800 g), $Cu(NO_3)_2{\cdot}3H_2O$ (0.006 mol, 1.449 g), and $Ni(NO_3)_2{\cdot}6H_2O$ (0.009 mol, 2.617 g) in distilled water (30 mL) was again prepared. Both of the solutions were sonicated for 30 min and were added dropwise to a vessel containing distilled water (30 mL) with vigorous stirring and adjusting pH = 10 by adding a suitable amount of sodium hydroxide solution. The slurry was continued to stir at ambient temperature for 30 min and subsequently aged at 353 K for 20 h. The resulting mixture was cooled to the room temperature and then filtered. Drying of the solid material in an oven (423 K) affords Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr layered double hydroxide system.

2.5. General Procedure for the Ring-Opening of Epoxides with Acetic Anhydride

In an experimental tube containing a magnetic stirrer, a solution of epoxide (1 mmol) in acetic anhydride (1 mL) was prepared. Next, Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH (0.07 g) was added and the reaction mixture was stirred under oil bath (353 K) conditions for an appropriate time. Progress of the reaction was monitored by TLC (eluent: *n*-hexane/EtOAc : 4/2). After the reaction was completed, the nanocatalyst was magnetically separated. An aqueous solution of $NaHCO_3$ (5 %, 5 mL) was then added and the resulting mixture was stirred for 5 min. The product was then extracted by EtOAc (2×5 mL) and then dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure affords the pure 1,2-diacetate in 81–95 % yield (Table 1).

3. Results and Discussion

3.1. Synthesis and Characterizations of Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH System

The study was started by the synthesis of Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr layered double hydroxide system *via* a three-step procedure. Primarily, magnetically nanoparticles of Fe_3O_4 were synthesized *via* a chemical co-precipitation of chloride salts of Fe^{2+} and Fe^{3+} in aqueous ammonia. Next, silica layer was coated on nanocores of Fe_3O_4 using tetraethyl orthosilicate at room temperature. Finally, the moiety of Cu-Ni-Fe-Cr layered double hydroxide was immobilized on silica layered magnetite using an in-situ growth procedure (Fig. 2). The prepared nanocomposite system was then characterized using SEM, EDX, XRD, TEM, and VSM analyses.

Scanning electron microscopy (SEM) technique as a primary tool was utilized to determine the size distribution and morphology of the surface in Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH system. The illustrated image in Fig. 3 shows that the particles were agglomerated to form granular segments with the size distribution from 21 to 37 nm and extremely porous surface. Based on the defined categories in literature, the prepared composite system is a mesoporous material.

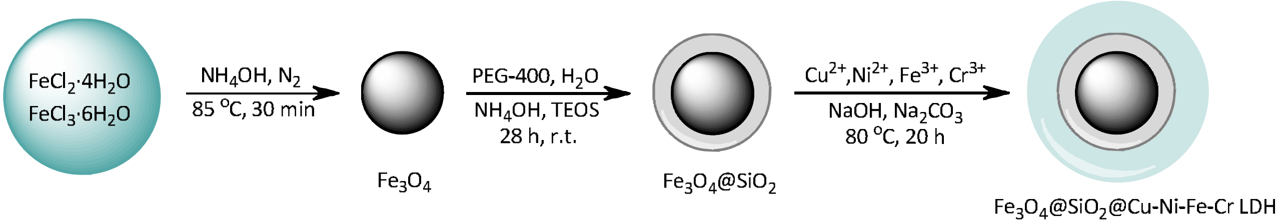


Fig. 2. Synthesis of Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH system

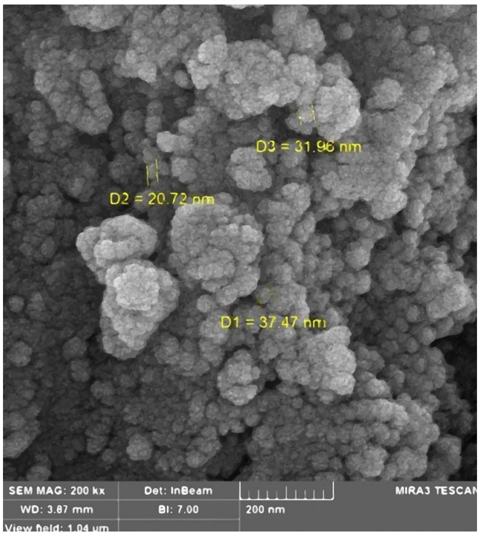
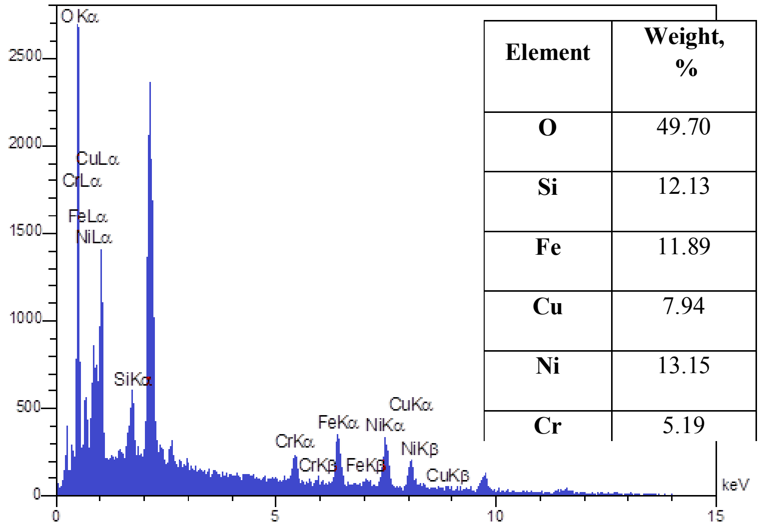


Fig. 3. SEM image of Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH system



Element	Weight, %
O	49.70
Si	12.13
Fe	11.89
Cu	7.94
Ni	13.15
Cr	5.19

Fig. 4. EDX of Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH system

Next, energy-dispersive X-ray (EDX) analysis was used to determine the elemental profile of Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH system. The depicted graph in Fig. 4 clearly shows that the elements of O, Si, Fe, Cu, Ni, and Cr are present in composition of the nanocatalyst. Based on this analysis, the immobilization of Cu-Ni-Fe-Cr LDH moiety on silica-layered Fe_3O_4 is successfully verified.

In continuation, the phase purity and crystallinity character of Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH system was determined using X-ray diffraction (XRD) analysis (Fig. 5).

The Figure represents the diffraction peaks at 2θ = 11.49°, 23.38°, 34.26°, 38.81°, 60.37°, and 61.73° corresponding to the crystal planes of (0 0 3), (0 0 6), (1 0 2), (1 0 5), (1 1 0), and (1 1 3), respectively. These characteristics are attributed to the green rust. The layered double hydroxide with a hexagonal crystallinity is in proper condition with the reference format ICSD 00-049-0723 (iron nickel chloride hydroxide hydrate). Furthermore, the graph represents a set of sharp symmetric peaks at low 2θ values representing the characteristic features of hydrotalcite-like materials.[39] The peaks at 2θ = 30.2°, 35.5°, 43.3°, 53.7°, 57.2°, and 62.9° are assigned to (0 2 2), (1 1 3), (0 0 4), (2 2 4), (1 1 5), and (0 4 4) crystal planes of Fe_3O_4 with high phase purity and crystallinity character of the standard one of cubic spinel magnetite (JCPDS No. 65-3107).[40,41] This analysis clearly demonstrates the successful immobilization of Cu-Ni-Fe-Cr LDH moiety on Fe_3O_4@SiO_2 compartments.

Structural analysis and the immobilization of Cu-Ni-Fe-Cr LDH moiety on nano cores of Fe_3O_4@SiO_2 was further investigated using transmission electron microscopy (TEM) technique. The illustrated images in Fig. 6 show that nanoparticles of Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH system are uniformly distributed and the core-shell concept of LDH on silica-layered magnetite is well demonstrated.

Finally, the magnetic behavior of Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH system was studied using vibrating sample magnetometer (VSM) analysis at the external applied magnetic field up to 20 kOe. The illustrated graph in Fig. 7 shows that the prepared nanocomposite exhibited the non-liner and reversible magnetic property without any hysteresis loop of magnetization. The literature review shows that the *s*-shape magnetic behavior is the characteristic feature of soft magnetic ma-terials. In addition, the saturation magnetization value of Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH system was measured 6 emu g^{-1}. Comparison of the magnetization value of Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH with that of Fe_3O_4@SiO_2 (30 emu g^{-1}) clearly shows that through the immobilization of non-magnetic moiety of Cu-Ni-Fe-Cr LDH on nano cores of silica-layered magnetite, the magnetic property is intensively decreased. Nevertheless, the magnetization value is still enough for any magnetic separation.

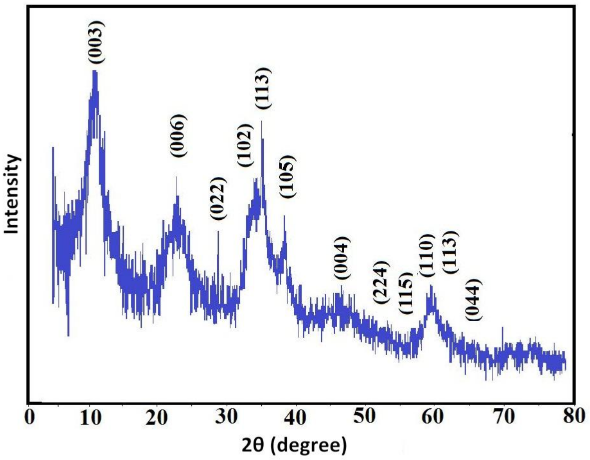


Fig. 5. XRD pattern of Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH system

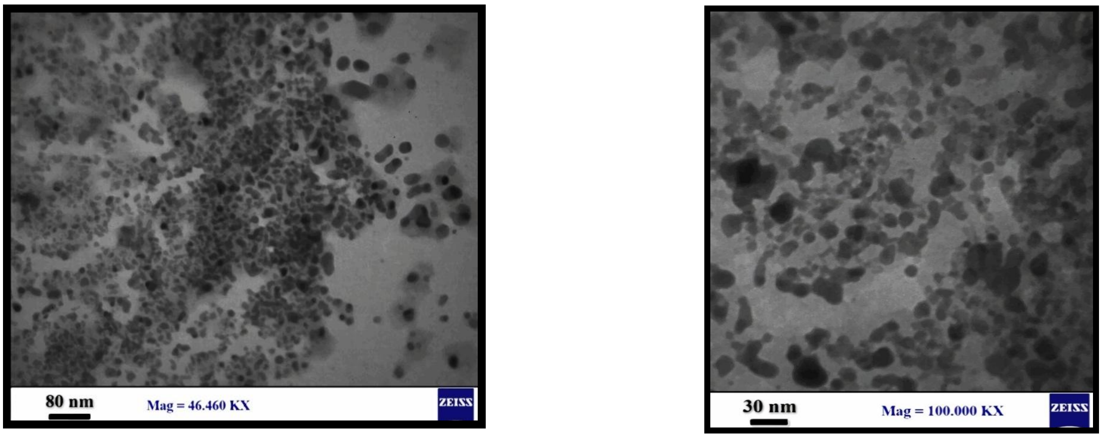


Fig. 6. TEM images of Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH system

3.2. Catalytic Ring-Opening of Epoxides to 1,2-Diacetates

After the successful synthesis and characterization of Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr layered double hydroxide system, we prompted to investigate nucleophilic ring-opening of epoxides to *vic*-diacetates with acetic anhydride in the presence of Fe_3O_4@SiO_2@LDH system. Primarily, the ring-opening of styrene oxide with acetic anhydride as a model reaction was carried out under different reaction conditions. The obtained results exhibited that the titled reaction in the absence of nanocatalyst was not taking place even at the prolonged reaction times. However, using a small amount of Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH system dramatically accelerated the rate of reaction. In this context, the evaluations for influence of reaction solvent, temperature, and amount of nanocatalyst represented that for the transformation of styrene oxide to corresponding *vic*-diacetate, using the nanocatalyst (70 mg) and acetic anhydride (1 mL) per 1 mmol of styrene oxide in oil bath (353 K) were the requirements to afford the product in high yield. Encouraged by the result, the suitability of this synthetic method was more studied using structurally diverse epoxides at the optimized reaction conditions. The results of this investigation are summarized in Table 1. The Table shows that all reactions were carried out successfully within 15–40 min to afford *vic*-diacetate in 81–95 % yield.

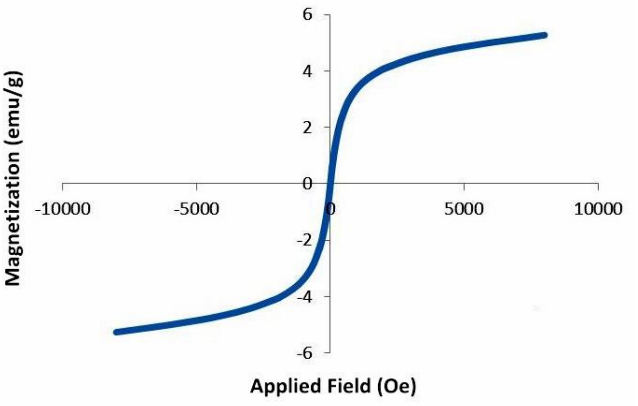
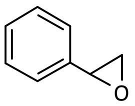
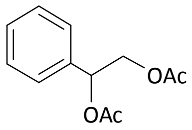
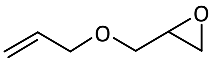
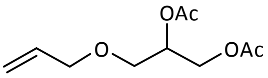
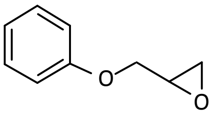
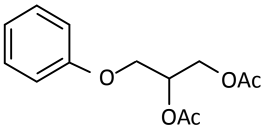
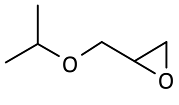
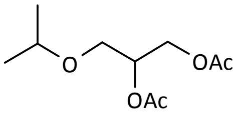
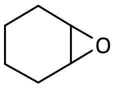
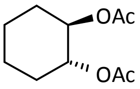
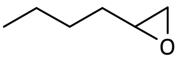
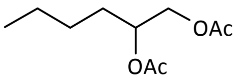
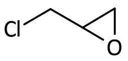
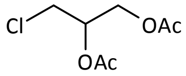
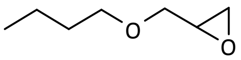
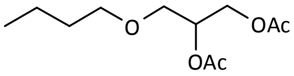


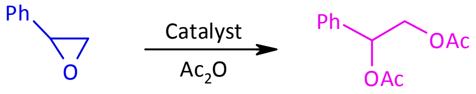
Fig. 7. Magnetic property of Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH system

Table 1. Conversion of epoxides to vic-diacetates catalyzed by Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH system[a]

Entry	Substrate	Product	Time, min	Yield, %[b]	Ref.
1			40	90	[24], [26]
2			30	86	[24], [26]
3			20	95	[24], [26]
4			40	89	[24], [26]
5			40	85	[24], [26]
6			30	81	[24], [26]
7			15	85	[24], [26]
8			20	91	[24], [26]

Notes: [a] All reactions were carried out under oil bath conditions (353 K) using 1 mmol of epoxide, Ac_2O (1 mL) and Fe_3O_4@SiO_2@ Cu-Ni-Fe-Cr LDH (0.07 g); [b] Yields refer to isolated pure products

Table 2. Comparison of styrene oxide conversion to 1,2-diacetoxy-1-phenylethane catalyzed by $Fe_3O_4@SiO_2@$Cu-Ni-Fe-Cr LDH and other reported reagents



Entry	Catalyst	Mol %	Condition	Time (h)	Yield (%)	Ref.
1	$Fe_3O_4@SiO_2@$Cu-Ni-Fe-Cr LDH	0.07 g	353 K	40 min	90	this work
2	HY Zeolite	0.05 g	r.t.	12	90	[22]
3	$LiClO_4$	50	r.t.	2–5	66	[23]
4	Molecular sieves 4 Å	0.15 g	Reflux	2	90	[24]
5	SbF_3	30	Reflux	2	89	[26]
6	$ZrO(OTf)_2$	0.75	323 K	1 min	99	[27]
7	$B(OH)_3$	200	Reflux	2	85	[28]
8	$NaOAc{\cdot}3H_2O$	200	343 K	2	96	[30]
9	Bu_4NCl	5	Reflux	3	83	[31]
10	Bu_3P	10	Reflux	24	98	[32]
11	$Er(OTf)_3$	0.1	r.t.	2	0	[33]

The suitability of this synthetic protocol was further studied by comparing the nucleophilic ring-opening of styrene oxide with acetic anhydride using $Fe_3O_4@SiO_2@$Cu-Ni-Fe-Cr layered double hydroxide and other reported catalyst systems (Table 2). Investigation of the titled protocols represents that $Fe_3O_4@SiO_2@$Cu-Ni-Fe-Cr LDH system in terms of the yield, reaction time and recycling capability shows a comparable or higher efficiently than the other systems.

3.3. Recycling of $Fe_3O_4@SiO_2@$Cu-Ni-Fe-Cr LDH System

The green and economic aspect of $Fe_3O_4@SiO_2@$ Cu-Ni-Fe-Cr LDH system was also studied by investigation of the reusability in nucleophilic ring-opening of styrene oxide with acetic anhydride at the optimized reaction conditions (Table 1, entry 1).

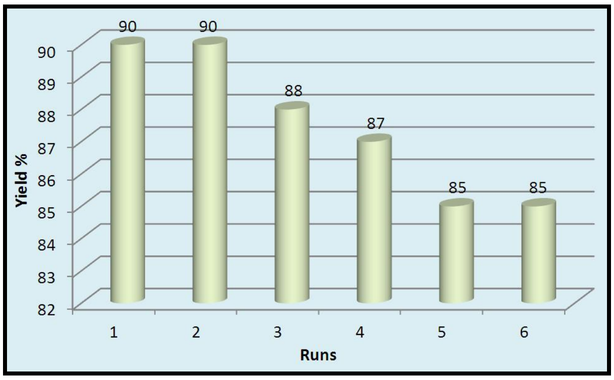


Fig. 8. Recycling of $Fe_3O_4@SiO_2@$Cu-Ni-Fe-Cr LDH system

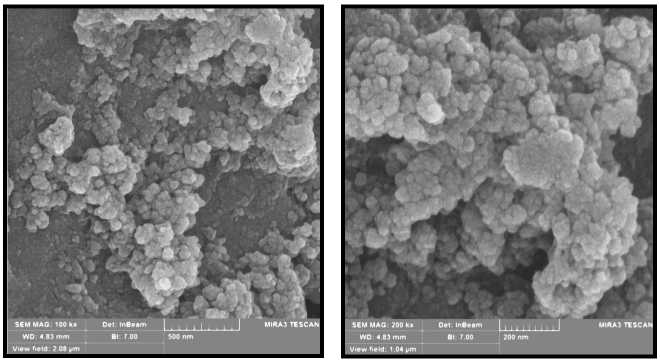


Fig. 9. SEM Images of First Recycled $Fe_3O_4@SiO_2@$Cu-Ni-Fe-Cr LDH System

Due to this, when the titled reaction was completed, the applied nanocomposite was magnetically separated from the reaction mixture, washed with EtOAc and then dried in an oven. The vessel of reaction was again charged with the fresh styrene oxide, acetic anhydride, and the recycled $Fe_3O_4@SiO_2@$Cu-Ni-Fe-Cr LDH system for the second run. Fig. 8 shows that $Fe_3O_4@SiO_2@$Cu-Ni-Fe-Cr LDH system can be reused for 6 consecutive cycles without the significant loss of its catalytic activity. In addition, SEM images of the first recycled magnetite-LDH system (Fig. 9) show that structure of the nanocatalyst remains intact.

4. Conclusions

In this paper, the immobilization of Cu-Ni-Fe-Cr layered double hydroxide moiety on silica-layered magnetite, $Fe_3O_4@SiO_2@$Cu-Ni-Fe-Cr LDH, was investigated. Structural elucidation of the magnetite-LDH was carried out using SEM, EDX, XRD, TEM, and VSM analyses. Next, catalytic activity of the composite system was investigated towards nucleophilic ring-opening of structurally diverse epoxides to the corresponding 1,2-diacetates. All reactions were carried out in acetic anhydride under oil bath (353 K) conditions within 15–40 min giving the products in 81-95 % yield. Reusability of the nanocomposite system was investigated for 6 recycling steps without the significant loss of the catalytic activity. This method represents several advantages in terms of high yields, short reaction times, lack of severe reaction conditions, simple work-up procedure, and easy separation of the nanocatalyst due to magnetic property.

Acknowledgements

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ШАРУВАТИЙ ПОДВІЙНИЙ ГІДРОКСИД Cu-Ni-Fe-Cr, ІММОБІЛІЗОВАНИЙ НА МАГНЕТИТІ З ШАРОМ КРЕМНІЮ, ЯК БАГАТОРАЗОВИЙ МЕЗОПОРИСТИЙ КАТАЛІЗАТОР ДЛЯ ПРАКТИЧНОГО ПЕРЕТВОРЕННЯ ЕПОКСИДІВ НА 1,2-ДІАЦЕТАТИ

Анотація. *Досліджено шаруватий подвійний гідроксид Cu-Ni-Fe-Cr (LDH), іммобілізований на шарі магнетиту ($Fe_3O_4@SiO_2@$Cu-Ni-Fe-Cr LDH) для розкриття кільця різних епоксидів оцтовим ангідридом з метою отримання віц-діацетатів протягом 15–40 хв із високим виходом. Багаторазове використання нано-LDH також вивчали протягом шести послідовних циклів без значних втрат каталітичної активності.*

Ключові слова: *Ac_2O, 1,2-діацетат, епоксид, $Fe_3O_4@SiO_2@$Cu-Ni-Fe-Cr LDH, розкриття кільця.*