Post-synthesis of manganese Schiff base complex
with Zr-based metal–organic framework immobilized
on Fe₃O₄ as a recyclable catalyst
for partial oxidation of cyclooctene

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Abstract:

A magnetic type of Zr-based UiO-66 metal-organic framework (Fe₃O₄@UiO-66-NH₂) was synthesized by co-precipitation and solvothermal method and then modified by a Schiff base reaction with salicylaldehyde. The Schiff base ligand was coordinated by manganese salt to develop a recyclable catalyst for mild oxidation of cyclooctene. The catalyst characterization was performed by the techniques of adsorption analysis (BET), X-Ray diffraction (XRD), Fourier transform IR spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and vibrating-sample magnetometer (VSM). Oxidation experiments were carried out in different reaction conditions such as reaction temperature and time, the amount of oxidant, and solvents. The catalyst exhibited good selectivity for the production of 2-cyclooctene-1-one. It was found that the conversion and selectivity decreased in the presence of methanol as a protic solvent in order to the strong interaction between oxygenated intermediates and solvent molecules. In addition, increasing the molar ratio of oxidant to feed led to a decrease in ketone selectivity and an increase in epoxy products. The allylic path was suggested as the dominant mechanism of cyclooctene oxidation via formation of cyclooctene 3-(tert-butyl) peroxide after oxidation of allylic C-H group and decomposition to form 2-cycloocten-1-one.

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1. Introduction

Partial oxidation of linear/cyclic hydrocarbons is a commercial method for the production of oxygenated compounds which are widely used to produce various types of chemical, food, pharmaceutical and petrochemical products [1]. Cyclooctene as an unsaturated cyclic hydrocarbon is commercially used to produce 8-ring oxygenated compounds which are consumed for the synthesis of amber and violet-smelling odorants. Cyclooctene is also consumed as an intermediate of 14-membered lactones [2] for the synthesis of antibacterial agents such as erythromycin and clarithromycin in clinical therapy [3].

Since the cyclic hydrocarbons show low activity in oxidation reactions, it is necessary to perform partial oxidation in the presence of suitable catalysts. Most of literatures have focused on the preparation of the catalysts with the high conversion and selectivity. Oxovanadium (IV) Schiff-base was covalently anchored on modified multi-wall carbon nanotubes (MWNTs) and used for the partial oxidation of cyclooctene in the presence of molecular oxygen [4]. 2-Cyclooctene-1-one, 2-cyclooctene-1-ol and epoxycyclooctane were the main products in acetonitrile. Catalytic oxidation of cyclooctene was investigated by means of a complex of manganese and iodosyl benzene [5]. Maximum yield (50%) was observed in molar ratios 1, 50, and 1000 for the catalyst, oxidant, and cyclooctene, respectively. Cobalt–based coordination polymer was synthesized by the reaction between cobalt salt and coupled sulfonic acid/bipyridine derivatives and found as an excellent catalyst for the oxidation of cyclooctene [6]. Maximum conversion was 80% after 24 h and epoxycyclooctane, 1,2 cyclooctanediol, and cyclooctenone were found as the main products. Tetra-n-butylammonium salts of Keggin and Wells–Dawson sandwich-type polyoxotungstates were synthesized and used for the oxidation of cyclooctene with H_2O_2 [7]. The yield of cyclooctenone was 35% after 24 h. Catalytic oxidation of cyclooctene and other organic compounds such as limonene and geraniol were investigated by means of sandwich tungstophosphates and H_2O_2 in acetonitrile [8]. A various types of epoxide were observed as the main oxygenated products with the different selectivities. A Schiff base ligand obtained by the reaction between salicylaldehyde and 1,2-cyclohexanediamine was chelated with Cu (II) and encapsulated in the zeolite-Y. The complex was used for the oxidation of different alkenes such as cyclooctene with tert-butylhydroperoxide (TBHP). Maximum conversion was found 89% with the selectivities 59 and 37% for epoxycyclooctane and cycloocten-1-one, respectively [9].

Manganese complexes containing different types of organic ligand have been interestingly used as the catalyst for the oxidation of cyclic hydrocarbons. A manganese-based coordination polymer with bipyridine and Dibenzoyl-L-tartaric acid was synthesized and used for the selective oxidation of cyclooctene. Maximum yield of ketone product (cyclooctenone) was 48% by use of 9.8 mmol oxidant and 1 mmol feed after 6 h. [10]. Results showed that the conversion increased by the time of reaction while the selectivity of ketone decreased. A derivative of manganese (III) porphyrin was grafted with hexahydroxytriptycene (HHT) resulting a microporous network polymer with high specific surface area [11]. The polymer demonstrated good reusability in the mild oxidation of cyclooctene and cyclohexene. Oxidation of cyclooctene, cyclohexene, styrene, and geraniol was studied by use of a manganese-substituted polyoxomolybdate complex and H_2O_2 as oxidant in acetonitrile. Cyclooctene oxide was observed as the main product in the case of oxidation of cyclooctene [12]. Kinetic modeling and experiments of cyclooctene oxidation with H_2O_2 on Mn-trimethy-triazacyclononane were performed [13]. A mechanism based on H_2O_2 activation on the surface of the complex was found as the rate-determining step. In addition, the ratio of productive to unproductive H_2O_2, catalyst deactivation, and the temperature were found as the important parameters of the reaction rate.

Metal-organic frameworks (MOF's) as a type of metal clusters contain coordination networks and demonstrate porous extended structure in three dimension. Because of high surface area, porosity, mechanical, and thermal resistance, the MOF's exhibit good ability to perform catalytic reactions [14-16]. Iron based metal organic framework Fe(BTC) has been applied for the partial oxidation cyclooctene and other cycloalkenes [17]. It was found that the type of the oxygenated product strongly depends on the nature of the substrate. The liquid phase oxidation of cyclooctene was studied over $Cu_3(BTC)_2$ at 75 $^\circ$C with TBHP in liquid toluene [18]. Maximum conversion was observed after 120 h (80%) with a good selectivity for epoxy product. Similar results were observed during the oxidation of cyclooctene over the first raw transition metallophthalocyanines [19]. UiO-66 as an archetypal MOF exhibits high specific surface area, high mechanical, thermal, acidic and water vapor stability [20]. It has been used as support of metallic catalysts for partial oxidation of alcohols [21], cyclohexene [22], and alkenes epoxidation [23].

Since most of the researches have been published on improving the activity and selectivity of the catalysts, fewer articles have been published on the preparation of catalysts that are capable of being recycled and reused. Application of the magnetic nanoparticles is an effective method to make the catalysts as recyclable and reusable samples. Magnetic UiO-66-NH$_2$ can be synthesized by solvothermal method [24, 25] and used in association of magnetic particles as decorated form which are fabricated by co-precipitation [26, 27] or layer by layer process [28]. In this work, we have been reported post-synthesis of UiO-66-NH$_2$ decorated by magnetic nanoparticles. The magnetic MOF is coordinated with manganese salt to form a recoverable catalyst for the partial oxidation of cyclooctene.

2. Experimental

2.1. Materials and Equipment

Ferrous chloride tetrahydrate (FeCl$_2$·4H$_2$O, >99%) and ferric chloride hexahydrate (FeCl$_3$·6H$_2$O, >99%), as well as the precursors of Fe$_3$O$_4$ and 2-aminoterephthalic acid (H$_2$BDC-NH$_2$, >99%) and Zirconium chloride (ZrCl$_4$, 99%) as well as the precursors of UiO-66-NH$_2$ and Manganese chloride (MnCl$_2$·4H$_2$O, >99%) were supplied by Merck. N, N-Dimethylformamide (DMF, >99.9%), salicylaldehyde (>99%), dry toluene (HPLC grade), acetonitrile (HPLC grade) and Methanol (HPLC grade) were purchased from Aldrich. Ultrapure water was obtained from Milli-Q Ultrapure Water (Millipore, USA).

Characterization of crystal phases in the MOF was performed by means of XRD pattern provided by a Philips PW800 X-ray equipment under Cu Kα radiation (λ=1.54 Å). A Philips XL-30 scanning electron micrograph (SEM) and CM120 instrument (TEM microscope) were used to determine morphology and particle size of MOF, respectively. Fourier transform infrared (FT-IR) measurement was done by an 8400S instrument (Shimadzu) to determine the functional groups in the coordinated ligand. The N$_2$ adsorption–desorption isotherms were obtained to determine the surface area and porosity of the magnetic MOF by a Micrometitis ASPS 2010 analyzer. Atomic analysis for leaching experiments was performed by ICP-OES (Perkin-Elmer, DV 5300). Analysis of the oxygenated products were carried out by a GC/Mass chromatograph (Agilent 6890) equipped by capillary column (HP-5 MS, 30 m) and mass detector (5973 N). Finally, magnetization curve of the sample was obtained from a vibrating sample magnetometer (VSM, MDK Co., Iran).

## 2.2. Preparation of decorated Fe$_3$O$_4$@UiO-66-NH$_2$

Fe$_3$O$_4$ as the magnetic phase of iron oxide was synthesized by co-precipitation method [26]. 4.86 g ferrous chloride tetrahydrate (FeCl$_2$·4H$_2$O) and 0.99 g ferric chloride hexahydrate (FeCl$_3$·6H$_2$O) were dissolved in deionized water (80 mL) in the presence of ammonia (6 mL, 25%) under nitrogen atmosphere. After 4 h, the sample was collected by a magnet and washed three times by the water. Fe$_3$O$_4$@UiO-66-NH$_2$ was prepared by solvothermal method [21]. 0.1 g Fe$_3$O$_4$ was added to 100 mL DMF and stirred in ultrasonic batch for 30 min. 0.424 g ZrCl$_4$ and 0.272 g 2-aminoterephthalic acid (H$_2$BDC-NH$_2$) were then added and stirred for 60 min at room temperature. The mixture was then transferred to a stainless steel Teflon-lined autoclave and kept at 120 °C. After 24 h, the sample was collected and washed three times by ethanol. The residual solvent was removed by use of a Soxhlet extractor.

2.3. Post-synthesis of decorated Fe$_3$O$_4$@UiO-66-NH-Sa

Post-synthesis of magnetic MOF was performed by Schiff base reaction between amine group of UiO-66-NH$_2$ and hydroxyl group of salicylaldehyde. Fe$_3$O$_4$@UiO-66-NH$_2$ was added to a solution containing 30 mL dry toluene and 2.5 mL salicylaldehyde and stirred at 80 °C under reflux condition. After 24 h, the sample (Fe$_3$O$_4$@UiO-66-NH-Sa) was collected by the magnet, washed three times by ethanol, and dried at 110 °C.

2.4. Synthesis of Fe$_3$O$_4$@UiO-66-NH-Sa@MnCl$_2$

0.5 g Fe$_3$O$_4$@UiO-66-NH-Sa was dispersed in 50 mL water in ultrasonic bath. 0.105 g MnCl$_2$·4H$_2$O was then added and stirred for 24 h at room temperature. In this way, Mn ions are coordinated with UiO-66-NH-Sa to form the heterogeneous catalyst (Scheme 1). The sample was then collected, washed by water and dried at 110 °C.
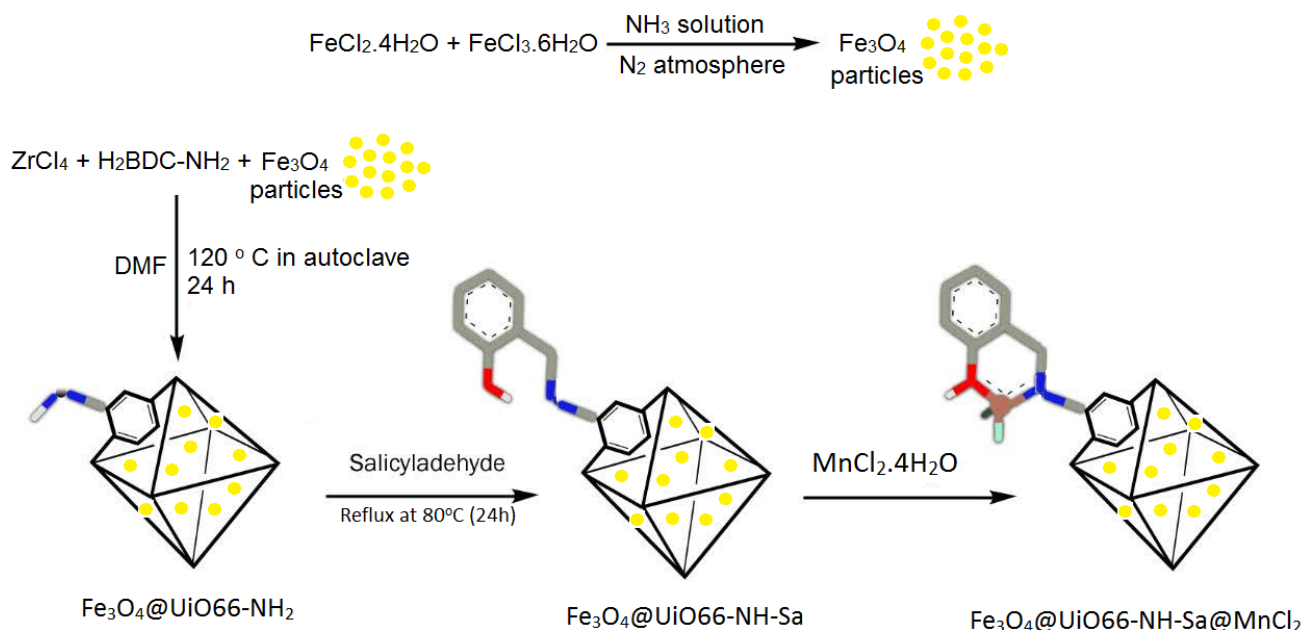
Scheme (1) Steps of Preparation of Fe$_3$O$_4$@UiO-66-NH-Sa@MnCl$_2$ by solvothermal method [21]

2.5. Catalytic reactions

Experiments of mild oxidation of cyclooctene were carried out in batch liquid conditions. Cyclooctene (Aldrich >99%) was introduced to a vessel with the certain amount of the solvent. The catalyst and oxidant were then added to the vessel and the mixture was stirred. After a certain period of time, the catalyst was collected by use of a magnet and the products were analyzed by means of GC/Mass chromatography equipped by capillary column, He as the carrier gas, and mass detector (5973 N). The injection, initial and final temperatures of the

column were 250, 70, and 250 ^oC (5 ^oC/min), respectively. Conversion and selectivity of the products were calculated by means of the following equations:

$$\%C_{total} = (mol_{clooctene} \text{ reacted} / mol_{clooctene} \text{ in the feed}) \times 100 \quad (1)$$

$$\%S_{pr.} = (mol_{clooctene} \text{ converted to pr.} / mol_{clooctene} \text{ reacted}) \times 100 \quad (2)$$

After each experiment, the catalyst was collected using external magnetic field, washed by a mixture of ethanol and water (1:1), dried and reused for the next oxidation reaction. After each run, the reaction solution was analyzed for leaching test by use of ICP-OES equipment.

3. Results and discussion

Figure 1 shows details of BET measurements for Fe_3O_4@UiO-66-NH-Sa. The surface area and mean pore diameter of magnetic MOF are 184.2 m^2/g 10.11 nm, respectively. Comparison of BET surface area of the sample with the pure UiO-66 [20] shows occupation of micropores in MOF structure after post-synthesis and catalyst preparation. Isotherm type IV is observed in adsorption-desorption diagram of Fe_3O_4@UiO-66-Sal with a hysteresis loop between p/p_o= 0.3 and 1 resulting formation of interconnected channels in MOF structure [26].
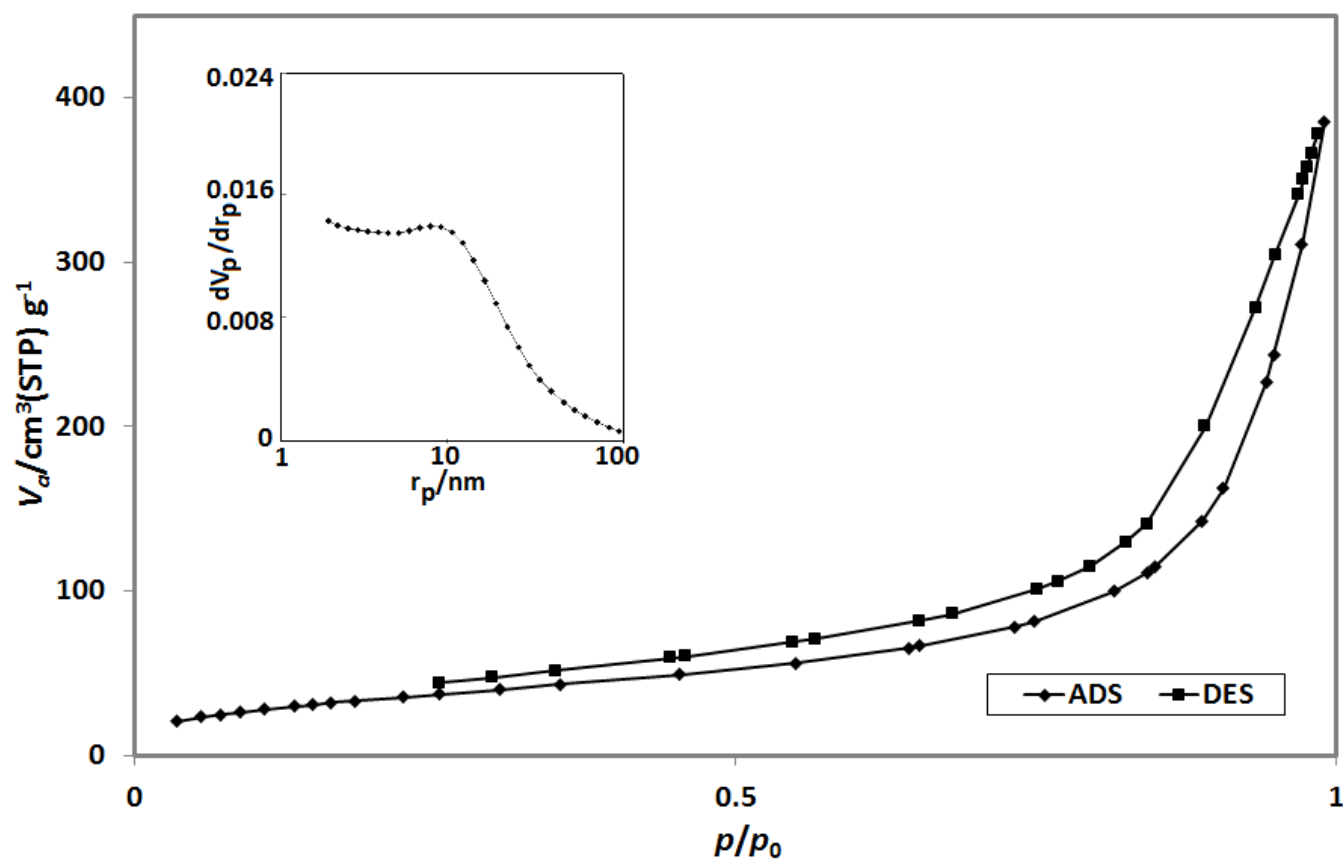

Figure 1: Diagram of N_2 adsorption–desorption and pore size distribution for Fe_3O_4@UiO-66-NH-Sa

XRD pattern of Fe_3O_4@UiO-66-NH-Sa is given in figure 2. The main sharp peak of UiO-66-NH_2 demonstrates at 7° that corresponds to the reflection sheet of d_{111}, similarly reported as the standard peak of UiO-66 [27]. It is observed that the main structure of MOF does not change during modification and post-synthesis procedure. The high intensity of the characteristic peak for UiO-66-NH_2 represents a highly crystalline structure of MOF. Other peaks are 8°, 26°, and 31° which are corresponded to the reflection sheets of d_{200}, d_{600}, and d_{711}, respectively. It can be also seen the main peaks of Fe_3O_4 containing reflection sheets appeared in 36°, 47°, 58° and 60° which are corresponded to the d_{311} and d_{400}, d_{511}, and d_{440} in the magnetic iron oxide, respectively [28].
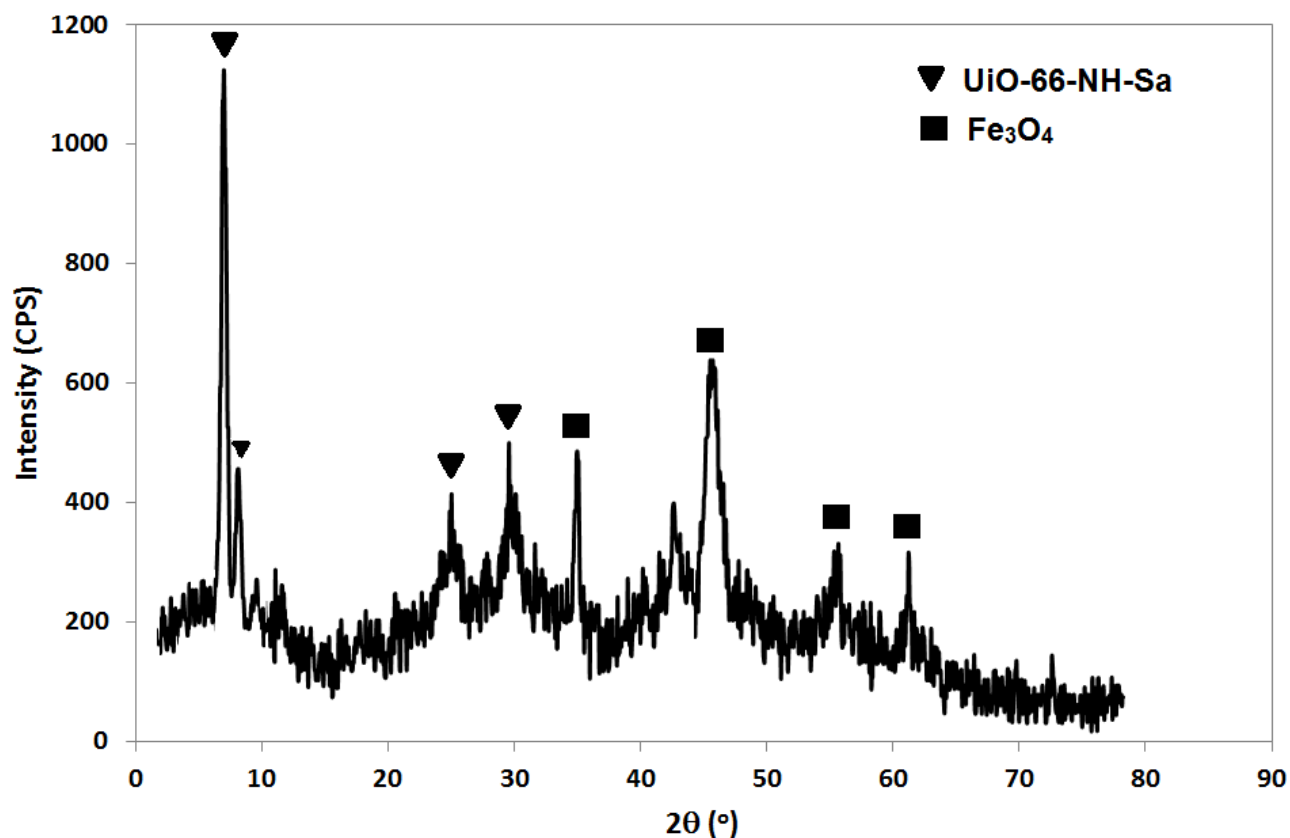
Figure 2: XRD pattern of Fe_3O_4@UiO-66-NH-Sa

Figure 3 illustrates FTIR spectra of Fe_3O_4@UiO-66-Sal and UiO-66-NH-Sa. The absorption bands of main functional groups in UiO-66-NH-Sa structure are marked on the figure. These peaks are 665, 769, 1257, 1435, and 1574 cm^{-1} which are assigned to O-H bending, C-H bendings, C-N stretching, -COOH symmetric and asymmetric stretching, respectively [29, 30]. Moreover, a new vibrational band appeared in 583 cm^{-1} can be assigned to the characteristic band of Fe_3O_4.
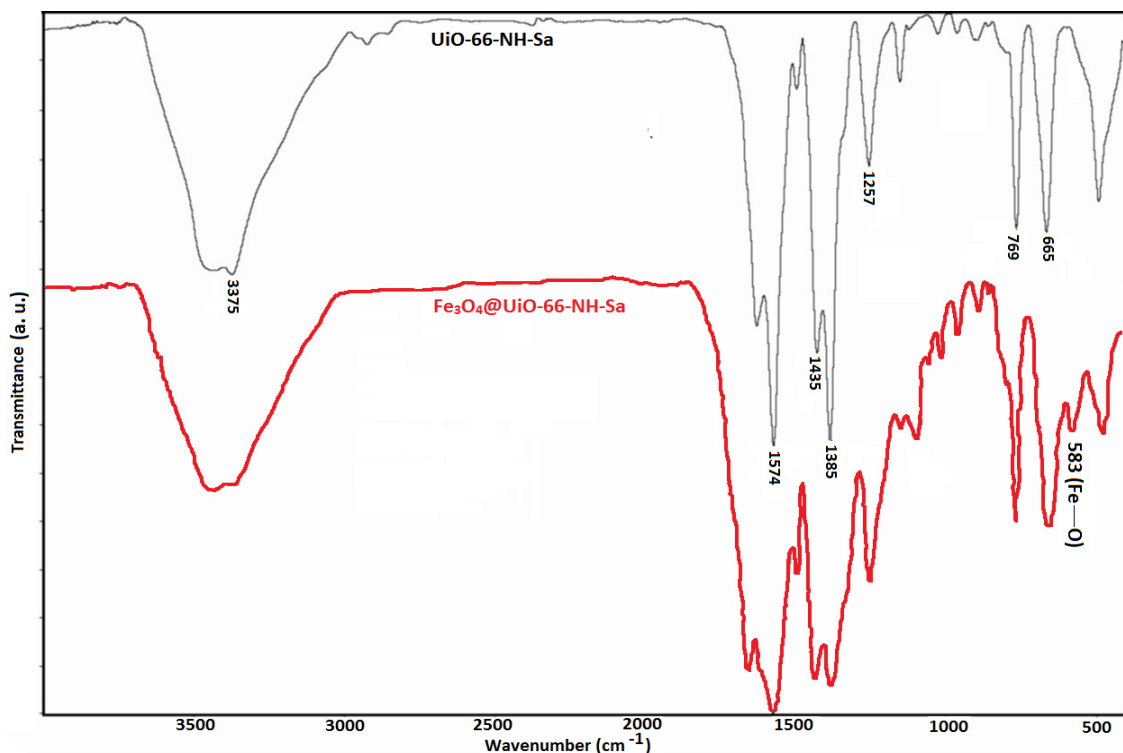
Figure 3: FTIR spectra of UiO-66-NH-Sa (top) and Fe$_3$O$_4$@UiO-66-NH-Sa (bottom)

Magnetization curve of Fe$_3$O$_4$@UiO-66-NH-Sa@MnCl$_2$ is given in figure 4. The sample exhibits small hysteresis loop and remnant magnetization indicating easy collection and re-dispersion of the sample during catalytic reaction by use of external magnetic field or removal of it.
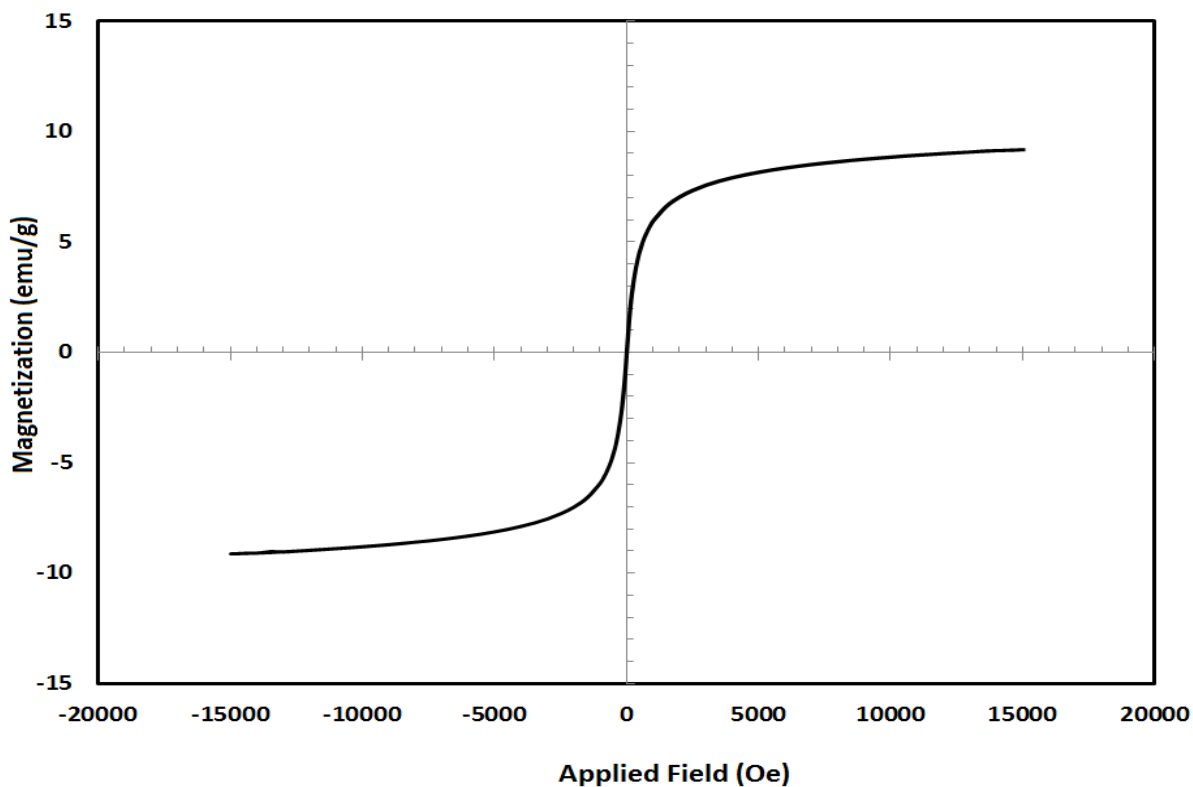

Figure 4: Magnetization curve of Fe$_3$O$_4$@UiO-66-NH-Sa@MnCl$_2$

Morphology of Fe_3O_4@UiO-66-NH-Sa@$MnCl_2$ particles are illustrated in figure 5. The particles are seen in the spherical shapes with the unique size, given in SEM images. According to TEM images of Fe_3O_4@UiO-66-NH-Sa@$MnCl_2$ and the particle size distribution, the size of Fe_3O_4@UiO-66-NH-Sa@$MnCl_2$ particles is between 10 and 40 nm with the average of 21 nm. The aggregation of particles could be due to the addition of manganese salt during the catalyst synthesis in aqueous solution.
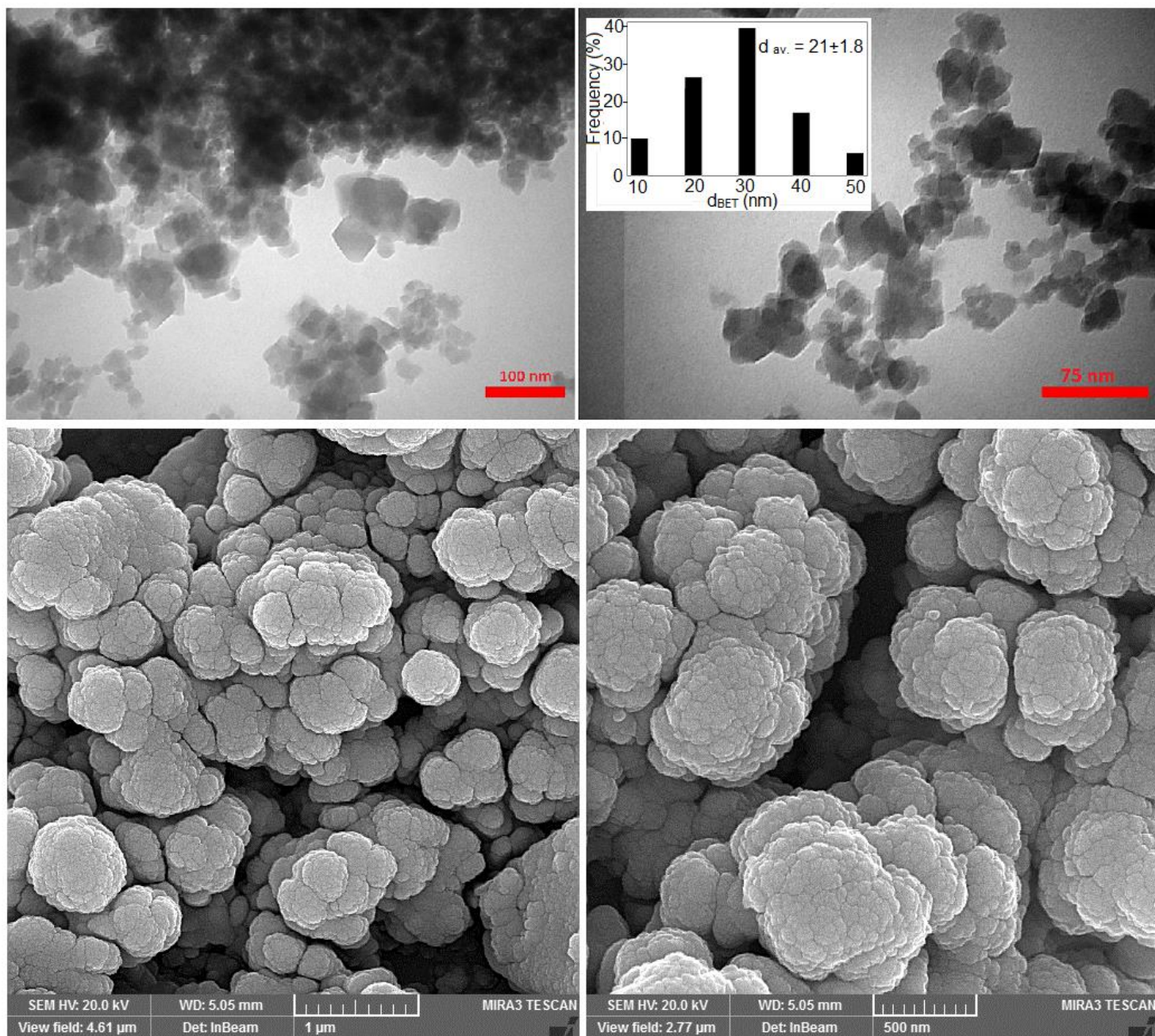
cyclooctene over MOF based catalysts is strongly affected by the temperature [18].
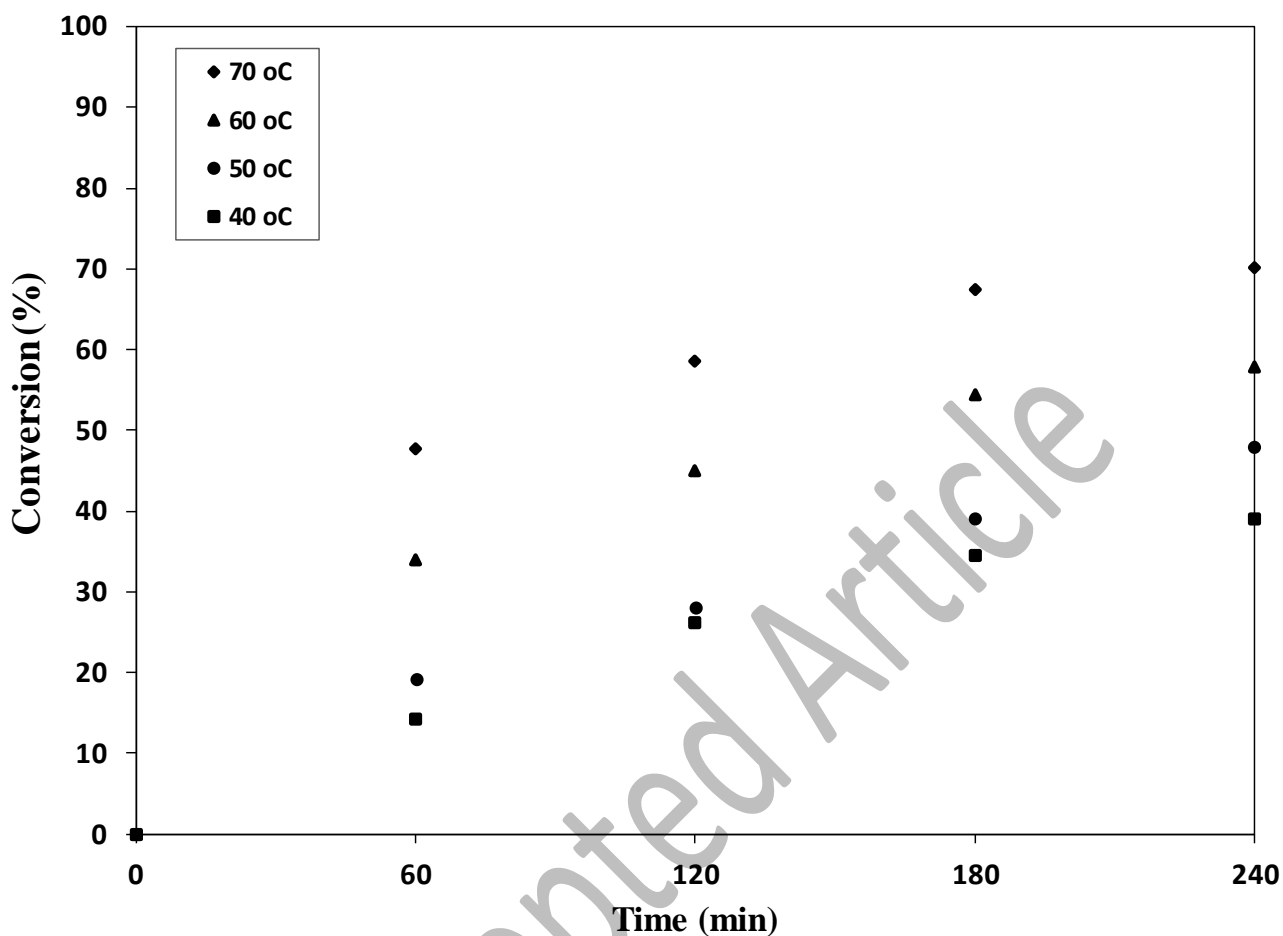
Figure 6: Conversion of cyclooctene oxidation over Fe_3O_4@UiO-66-NH-Sa@$MnCl_2$ as a function of temperature and time of reaction (Oxidant: TBHP= 5 mmol, $m_{catalyst}$ = 0.01 g, Solvent: acetonitrile, Cyclooctene: 5 mmol)

Selectivity of the products as a function of reaction temperature is shown in figure 7. It is observed that the main product is 2-cyclooctene-1-one with a selectivity of 61-74% in the temperature range of 40-70 °C. Another product is 2-cyclooctene-1-ol by the selectivity range of 18-10% in temperatures between 40 °C and 70 °C K, respectively. Finally, 1,2-epoxycyclooctane (cyclooctene oxide) is the third product with the selectivity 9~11%. Other products (such as cyclooctanone) were observed with low selectivity (less than 7%). Comparison of details obtained from the conversion and selectivity indicates that the effect of temperature on catalytic activity is greater than the selectivity. In other word, catalytic behavior of the MOF based manganese catalyst is similar at different temperatures.
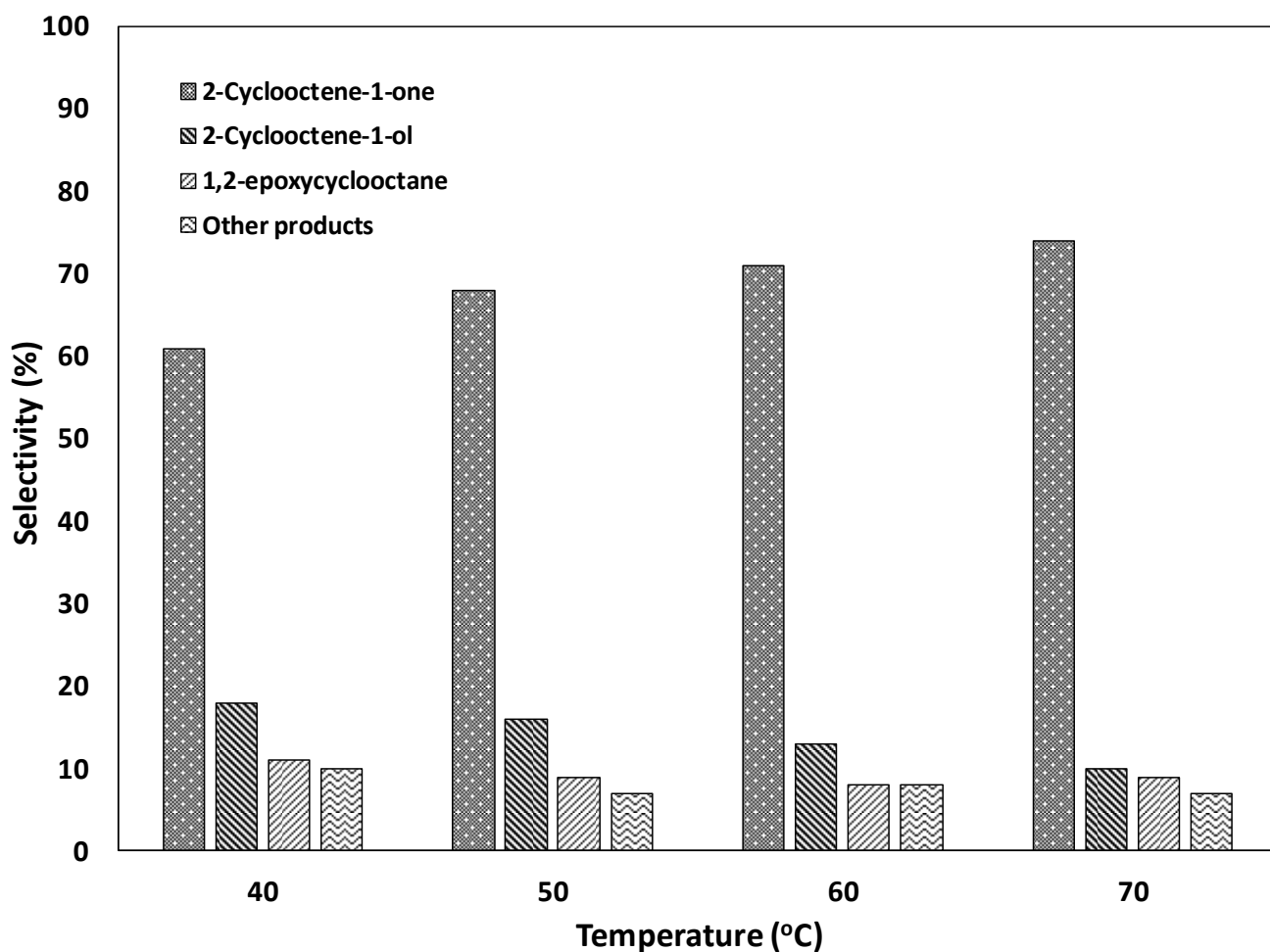
Figure 7: Selectivity of the products of cyclooctene oxidation over $Fe_3O_4@UiO-66-NH-Sa@MnCl_2$ in (Oxidant: TBHP= 5 mmol, $m_{catalyst}$ = 0.01 g, Solvent: acetonitrile)

Table 1 demonstrates details of oxidation of cyclooctene in acetonitrile as an aprotic solvent and methanol as a protic one. Results of the isolated yield (activity×selectivity) show that the maximum of yield for 2-cyclooctene-1-one is 51.8 which is observed at T= 70 °C in acetonitrile. It is also observed that the yield of reaction in acetonitrile is higher than methanol. For example, the yields of 2-cyclooctene-1-one in methanol in the temperatures 40, 50, 60, and 70 °C are and 13.3, 15.0, 19.7, and 25.5% while the yields of ketone product in acetonitrile and similar temperatures are 24.4, 31.2, 39.9, and 51.8%, respectively. It has been reported that the solvent polarity and basicity are two effective factors in the reactions of catalytic oxidation of cycloalkenes [31]. It has been also reported that acetonitrile is the best aprotic solvent to produce ketone product. In addition, methanol as a protic solvent can form hydrogen bond with the oxygenated intermediates resulting increase of their stability and reduce the overall reaction rate [31]. Another parameter that can affect the yield of reaction is the amount of oxidant or the molar ratio between oxidant and cyclooctene. Details of table 1 show that by increasing the amount of oxidant from 5 to 10 mmol, the yield of 2-cyclooctene-1-one decreases and the yield of other products increases. This observation is more noticeable at higher temperatures. It is also observed that the main product in the presence of oxidant alone (without any catalyst) is epoxycyclooctane with the yield of 17.4% and 20% in acetonitrile and methanol, respectively. It can be concluded that the MOF based catalyst plays a key role in determining the dominant mechanism.

Table: 1 Results of cyclooctene oxidation over $Fe_3O_4@UiO-66-NH-Sa@MnCl_2$ in different reaction conditions [a]

Entry	Temperature of reaction	Solvent of reaction	Oxidant amount	isolated Yield of main products (%)		
				epoxycyclooctane	2-cycloocten-1-one	2-cycloocten-1-ol
1	40 °C	Methanol	5 mmol	5.3	13.3	1.4
2	50 °C	Methanol	5 mmol	6.0	15.0	1.8
3	60 °C	Methanol	5 mmol	9.8	19.7	2.1
4	70 °C	Methanol	5 mmol	10.1	25.5	5.0
5	40 °C	Methanol	10 mmol	9.8	9.0	1.5
6	50 °C	Methanol	10 mmol	11.5	11.6	2.8
7	60 °C	Methanol	10 mmol	157	13.7	5.0
8	70 °C	Methanol	10 mmol	18.2	15.1	5.9
9	40 °C	Acetonitrile	5 mmol	4.4	24.4	2.0
10	50 °C	Acetonitrile	5 mmol	4.8	31.2	2.8
11	60 °C	Acetonitrile	5 mmol	5.7	39.9	4.0
12	70 °C	Acetonitrile	5 mmol	7.0	51.8	4.9
13	40 °C	Acetonitrile	10 mmol	5.0	23.8	4.4
14	50 °C	Acetonitrile	10 mmol	8.8	27.7	5.0
15	60 °C	Acetonitrile	10 mmol	14.5	29.3	8.6
16	70 °C	Acetonitrile	10 mmol	21.9	26.6	13.9
17 [b]	70 °C	Acetonitrile	5 mmol	18.2	0.5	0.4
18 [c]	70 °C	Methanol	5 mmol	15.0	0.4	0.1

[a] cyclooctene: 5 mmol, solvent volume: 5 mL, reaction time: 4 h, catalyst amount: 0.01 g, type of oxidant: TBHP

[b, c] no catalyst was used

According to the literatures, there are two pathways for the reaction progress (Scheme 2) [32]:

I) Allylic path including initially formation of cyclooctene 3-(tert-butyl) peroxide created by oxidation of allylic C-H group and finally decomposition to form 2-cycloocten-1-ol or 2-cycloocten-1-one. Increase of temperature enhance creation of carbonyl group instead of hydroxyl one.

II) Epoxidation path: In this pathway, oxidation of C=C bond leads to the reaction between 2-cycloocten-1-hydroperoxide and another molecule of cyclooctene and consequently production of cyclooctene oxide.

It can be seen that the dominant pathway of the reaction is Allylic path. In addition, it has been reported that Lewis acidic sites in MOF plays important role in the reaction progress [32]. These sites facilitate activation of peroxy group in the oxidant to attack allyl bond in cyclooctene.
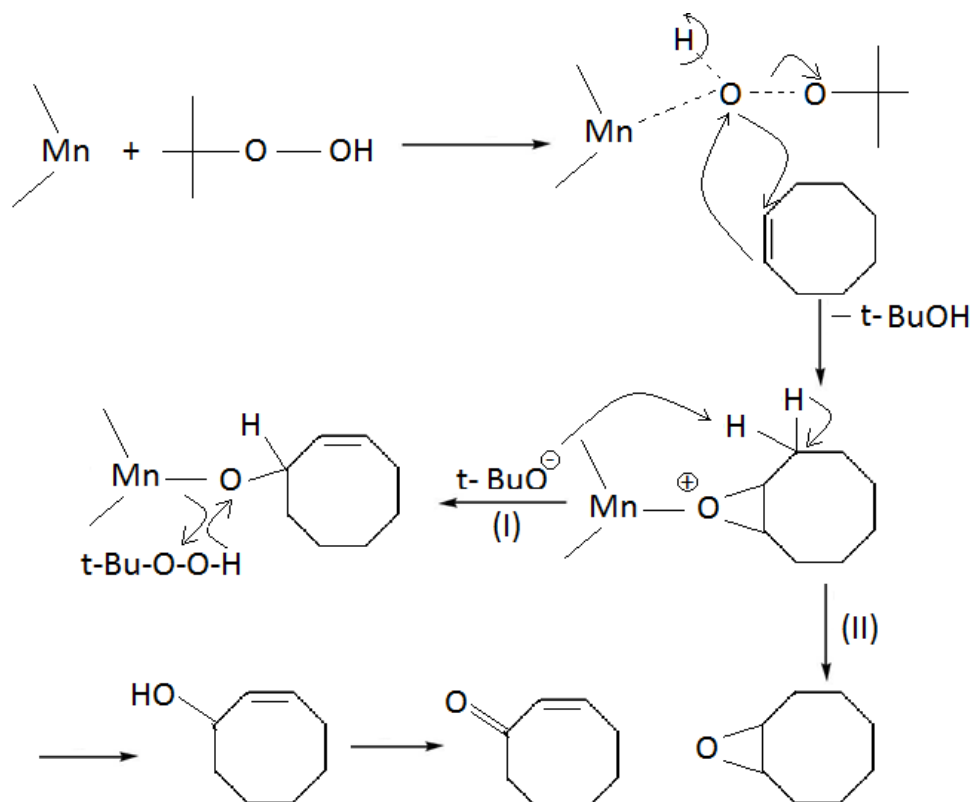
Scheme 2: Two main pathways of oxidation of cyclooctene: allylic path (I) and epoxidation path (II)

For the oxidation of unsaturated cyclic hydrocarbons over organometallic catalysts, various parameters have been introduced such as structure of ligand, physiochemical properties of support, type of transition metal, solvent effect, type of oxidant, etc. [18]. It has been generally accepted that the formation of peroxometalates or polyoxometalates (POMs) are the main intermediates of cycloalkenes oxidation over organometallic catalysts. The POMs are generally encapsulated in the pores of MOF and introducing second metal to the lattice enhances electron donors and oxidation sites in the structure of MOFs. Thus, presence of Mn sites promotes oxidation reaction by increase of the Lewis acidity acting as effective parameter for the peroxide ion activation and higher polarization of peroxy O-O bond [33].

Figure 8 shows details of reusability for 4 runs of cyclooctene oxidation over Fe_3O_4@UiO-66-NH-Sa@$MnCl_2$. It is observed that the values of loss for the conversion are 2.5, 1.8, 1.2, and 0.8% after 1th, 2th, 3th, and 4th runs, respectively. In other words, it is seen that the loss of conversion and yield of ketone product after 4 runs is 6% and 4.5%, respectively. In addition, it is observed that the amounts of metal loss by leaching after 1th, 2th, 3th, and 4th runs are 4.4, 2.0, 1.7 and 1.5 %, respectively. A significant change of the activity after first run can be related to the higher amount of leaching after run 1 but not much change is noticeable in other cases.
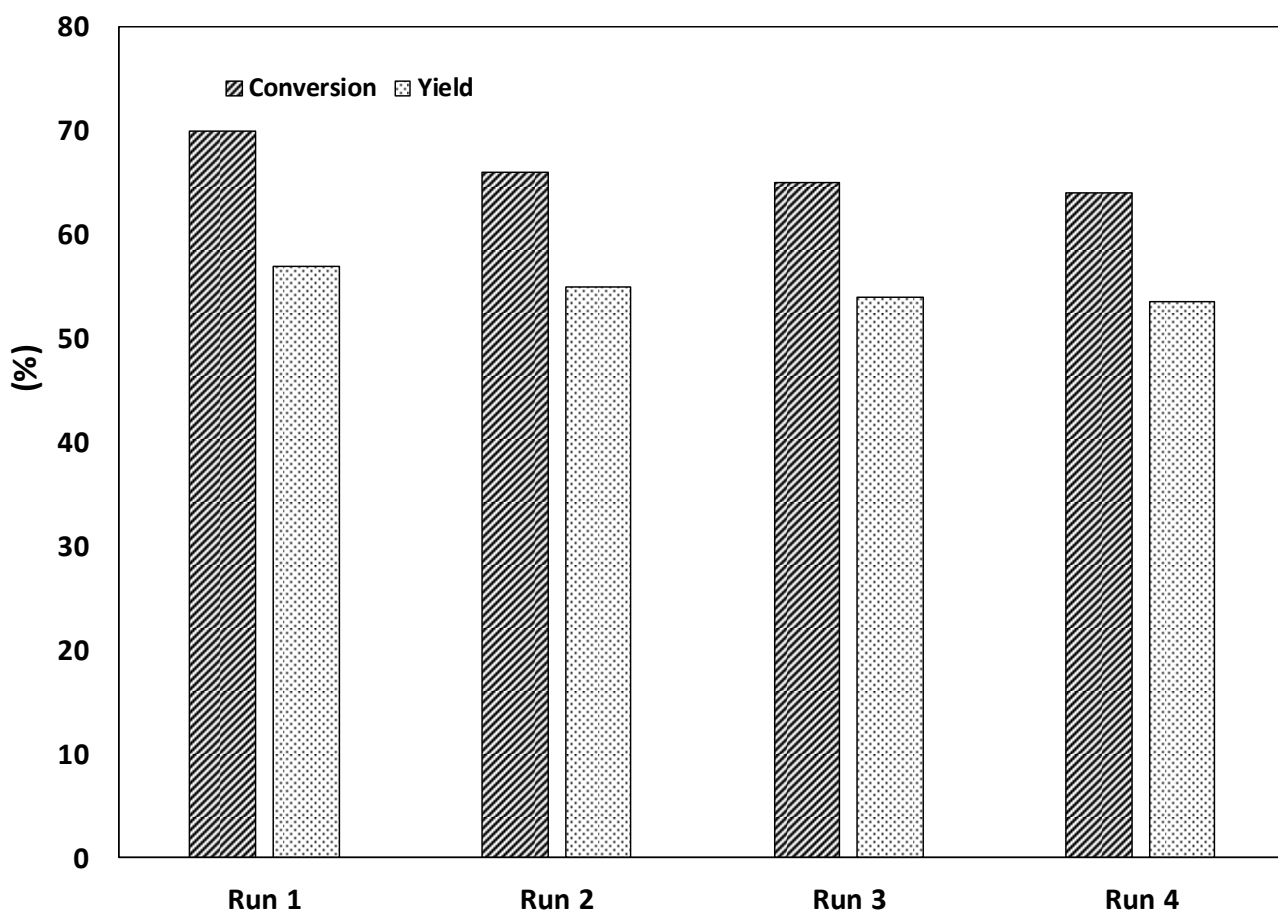
Figure 8: Details of reusability of Fe_3O_4@UiO-66-NH-Sa@$MnCl_2$ for the oxidation of cyclooctene

A comparison of catalytic activity between some heterogeneous catalysts for the oxidation of cyclooctene to 2-cyclooctene-1-one is presented in table 2. It can be seen that the Fe_3O_4@UiO-66-NH-Sa@$MnCl_2$ catalyst demonstrates good activity to oxidize cyclooctene and prepare ketone product.

Table 2 Comparison of experimental results for oxidation of cyclooctene over different catalysts

metal	ligand/support	oxidant	temp (^{o}C)	time (h)	yield (%)	solvent	ref.
V	MWNT	O_2	80	96	39.0	acetonitrile	[4]
Co	copolymer	TBHP	80	NA	3.5	-	[6]
W	Schiff base	TBHP	80	24	35.0	acetonitrile	[7]
Fe	polyoxotungstates	H_2O_2	50	6	47.8	acetonitrile	[8]
Mn	Schiff base	TBHP	80	4	6.0	-	[9]
Mn	copolymer	TBHP	80	6	48	-	[10]
Au NP	-	TBHP	100	10	2	acetonitrile	[35]
V	Schiff base	TBHP	85	16	21.3	acetonitrile	[36]
Mn NP	-	TBHP	70	4	12	acetonitrile	[37]
Mn	Modified Uio-66	TBHP	70	4	52.0	acetonitrile	this work

4. Conclusion

Fe$_3$O$_4$@UiO-66-NH-Sa@MnCl$_2$ as a recoverable catalyst was successfully synthesized and applied for the oxidation of cyclooctene in liquid phase condition. The catalyst exhibited significant activity for the production of oxygenated compounds, especially 2-cyclooctene-1-one and high reusability and recyclability. Maximum conversion and selectivity of ketone products were 70.2% and 74% at 70 ℃ after 4 h, respectively. It was found that the experiments in the presence of acetonitrile as an aprotic solvent exhibited better activity and selectivity for the production of 2-cyclooctene-1-one and the use of the protic solvent such as methanol decreased the conversion due to the formation of hydrogen bond with the oxygenated intermediates and reduction of the overall reaction rate. It was also observed that maximum yield of reaction was obtained by increasing the temperature and using an equal amount of oxidant and cyclooctene. It was suggested the allylic path as the dominant mechanism of oxidation of cyclooctene including formation of cyclooctene 3-(tert-butyl) peroxide after oxidation of allylic C-H group and decomposition to form 2-cycloocten-1-one.

Competing interests: The authors declare that they have no competing interests.

References:

[1] Uraz C., Atalay S., V$_2$O$_5$-MoO$_3$ Catalysts Preparation and Performance Testing on the Oxidation of Benzene to Maleic Anhydride in a Fixed Bed Reactor, *Iran. J. Chem. Chem. Eng*., **31**:9-13 (2012).

[2] Burevschi, E., Peña, I., Sanz, M. E., Medium-sized rings: Conformational preferences in cyclooctanone driven by transannular repulsive interactions. *Physical Chemistry Chemical Physics*, *21:*4331 (2019).

[3] Janas A., Przybylski P., 14-and 15-membered lactone macrolides and their analogues and hybrids: Structure, molecular mechanism of action and biological activity, *European j. Medicinal Chem*., **182:**111662 (2019).

[4] Salavati-Niasari M., Badiei A., Saberyan K., Oxovanadium (IV) salophen complex covalently anchored to multi-wall carbon nanotubes (MWNTs) as heterogeneous catalyst for oxidation of cyclooctene, *Chem. Eng. J*., **173:**651-658 (2011).

[5] Wegermann, C. A., Ribeiro, R. R., Ucoski, G. M., Nakagaki, S., Nunes, F. S., Drechsel, S. M., Study of the catalytic activity of non-heme manganese complexes toward oxidation of cyclooctene and cyclohexene, *Applied Catal. A*, **471**: 56-62 (2014)

[6] Zhang G., Shi Y., Wei Y., Zhang Q., Cai, K., Two kinds of cobalt–based coordination polymers with excellent catalytic ability for the selective oxidation of cis-cyclooctene, *Inorg. Chem. Commun*., **86**:112-117 (2017).

[7] Riahi Farsani M., Jalilian F., Yadollahi B., Amiri Rudbari H., Comparison between various Keggin and Wells–Dawson sandwich-type polyoxometalates in catalytic oxidation of cyclooctene and cyclohexene with hydrogen peroxide, *Appl. Organometallic Chem.*, **29**:7-11 (2015).

[8] Santos I. C., Gamelas J. A., Duarte T. A., Simoes M. M., Neves M. G. P., Cavaleiro J. A., Cavaleiro A. M., Catalytic homogeneous oxidation of monoterpenes and cyclooctene with hydrogen peroxide in the presence of sandwich-type tungstophosphates $[M_4(H_2O)_2 (PW_9O_{34})_2]^{n-}$, M= Co^{II}, Mn^{II} and Fe^{III}, *J. Mol. Catal. A: Chemical*, **426**: 593-599 (2017).

[9] Lashanizadegan M., Shayegan S., Sarkheil M., Copper (II) complex of (±) trans-1, 2-cyclohexanediamine azo-linked Schiff base ligand encapsulated in nanocavity of zeolite–Y for the catalytic oxidation of olefins, *J. Serb. Chem. Soc.*, **81**:153-162 (2016).

[10] Zhang G., Shi Y., Wei Y., Zhang Q., Zhang Y., Cai K., Xiu S., Synthesis of a pair of homochiral manganese-based coordination polymers as stable catalyst for the selective oxidation of cis-cyclooctene, *Inorg. Chem. Commun.*, **91**:81-84 (2018).

[11] Antonangelo A. R., Bezzu C. G., Mughal S. S., Malewschik T., McKeown N. B., Nakagaki S. A., porphyrin-based microporous network polymer that acts as an efficient catalyst for cyclooctene and cyclohexane oxidation under mild conditions, *Catal. Commun.*, **99**:100-104 (2017).

[12] Duarte T. A., Santos I. C., Simoes M. M., Neves M. G. P., Cavaleiro A. M., Cavaleiro, J. A., Homogeneous catalytic oxidation of olefins with hydrogen peroxide in the presence of a manganese-substituted polyoxomolybdate, *Catal. let.*, **144**:104-111 (2014).

[13] Bjorkman K. R., Schoenfeldt N. J., Notestein J. M., Broadbelt L. J., Microkinetic modeling of cis-cyclooctene oxidation on heterogeneous Mn–tmtacn complexes, *J. Catal.*, **291**:17-25 (2012).

[14] Hamidipour L., Farzaneh F., Cobalt metal organic framework as an efficient heterogeneous catalyst for the oxidation of alkanes and alkenes. *Reac. Kinet. Mech. Cat.*, **109**:67 (2013)

[15] Xie Y-Q., Zhang Y-M., Li Z-H., Yao H., Wei T-B., Shi B-B., Qu W-J., Lin Q., Synthesis, crystal structure of a novel metal–organic framework and its catalyzing properties on the selective oxidation of cyclohexene to cyclohexenone. *Inorg Chim Acta,*, **525:**120494, (2021).

[16] Flores J. G., Aguilar-Pliego J., Martin-Guaregua N., Ibarra I. A., Sanchez-Sanchez M., Room-temperature prepared bimetallic nanocrystalline MOF-74 as catalysts in the aerobic oxidation of cyclohexene., *Catal Today*, **394**: 295-303 (2022).

[17] Dhakshinamoorthy A., Alvaro M., Garcia H., Aerobic oxidation of cycloalkenes catalyzed by iron metal organic framework containing N-hydroxyphthalimide, *J. Catal.*, **289**:259-265 (2012).

[18] Junghans, U., Suttkus, C., Lincke, J., Lässig, D., Krautscheid, H., Gläser, R., Selective oxidation of cyclooctene over copper-containing metal-organic frameworks, Microporous Mesoporous Mater., **216**:151–160 (2015).

[19] Piroozmand, M., Safari, N., Samadi, A. A., Catalyzed oxidation of cyclohexene and cyclooctene with first row transition metallophthalocyanines, *Iran. J. Chem. Chem. Eng.*, **40**:85-89 (2006).

[20] Winarta J., Shan B., Mcintyre S. M., Ye L., Wang C., Liu J., Mu B., A Decade of UiO-66 Research: A Historic Review of Dynamic Structure, Synthesis Mechanisms, and Characterization Techniques of an Archetypal Metal–Organic Framework, *Cryst. Growth,* **20**: 1347-1362 (2020).

[21] Hou J., Luan Y., Tang J., Wensleya A. M., Yang M., Lu Y., Synthesis of UiO-66-NH$_2$ derived heterogeneous copper (II) catalyst and study of its application in the selective aerobic oxidation of alcohols. *J Mol Catal A: Chemical*, **407**: 53-59 (2015).

[22] Nguyen H. G. T., Mao L., Peters A. W., Audu C. O., Brown Z. J., Farha O. K., Hupp J. T., Nguyen S. B. T., Comparative study of titanium-functionalized UiO-66: support effect on the oxidation of cyclohexene using hydrogen peroxide, *Catal. Sci. Technol.,* **5**:4444 (2015).

[23] Kardanpour R., Tangestaninejad S., Mirkhani V., Moghadam M., Mohammadpoor I., Zadehahmadi F., Efficient alkene epoxidation catalyzed by molybdenyl acetylacetonate supported on aminated UiO-66 metal−organic framework, *J. Solid. State Chem.,* **226**:262-272 (2015).

[24] Shahin R., Yousefi M., Ziyadi H., Bikhof M., Hekmati M., pH-Responsive and magnetic Fe3O4@ UiO-66-NH2@ PEI nanocomposite as drug nanocarrier: Loading and release study of Imatinib, *Inorg. Chem. Commun*., **147**: 110186 (2023).

[25] Hejji L., Azzouz A., Pérez-Villarejo L., Castro E., Souhail B., Rodríguez-Castellón E., Fe3O4@ UiO-66-NH2 based on magnetic solid phase extraction for determination of organic UV filters in environmental water samples, *Chemosphere*, **341**: 140090 (2023).

[26] Li C. Y., Liu J. M., Wang Z. H., Lv S. W., Zhao N., Wang S., Integration of Fe3O4@ UiO-66-NH2@ MON core-shell structured adsorbents for specific preconcentration and sensitive determination of aflatoxins against complex sample matrix, *J. hazard. mater*., **384**:121348 (2020)

[27] Tripathy S. P., Subudhi S., Das, S., Ghosh M. K., Das M., Acharya R., Parida K., Hydrolytically stable citrate capped Fe3O4@ UiO-66-NH2 MOF: A hetero-structure composite with enhanced activity towards Cr (VI) adsorption and photocatalytic H2 evolution, *J. Colloid Interface Sci*., **606**:353-366 (2022).

[28] Chen R., Tao C. A., Zhang Z., Chen X., Liu Z., Wang J., Layer-by-layer fabrication of core–shell Fe3O4@ UiO-66-NH2 with high catalytic reactivity toward the hydrolysis of chemical warfare agent simulants. *ACS Appl. Mater. Interfaces*, **11**:43156-43165 (2019)

[29] He Q., Chen Q., Lu M., Liu X., Adsorption Behavior of Rhodamine B on UiO-66, *Chinese. J. Chem. Eng*., **22**: 1285-1290 (2014).

[30] Fiaz M., Athar M., Enhancing the Hydrogen and Oxygen Evolution Reaction Efficiency of Amine Functionalized MOF NH_2-UiO-66 via Incorporation of CuO Nanoparticles, *Catal. Lett.*, **150**:3314-3326 (2020)

[31] Cao Y., Yu H., Wang H., Peng F., Solvent effect on the allylic oxidation of cyclohexene catalyzed by nitrogen doped carbon nanotubes, *Catal. Commun*., **88**:99-103 (2017).

[32] El-Korso S., Khaldi I., Bedrane S., Choukchou-Braham A., Thibault-Starzyk F., Bachir R., Liquid phase cyclohexene oxidation over vanadia based catalysts with tert-butyl hydroperoxide: Epoxidation versus allylic oxidation. *J. Molecular Catal. A*, **394**:89-96 (2014).

[33] Lane B. S., Burgess, K., Metal-catalyzed epoxidations of alkenes with hydrogen peroxide. *Chem. Rev.*, **103**:2457 (2003).

[34] Guo Z., Zhou C., Hu S., Chen Y., Jia X., Lau R., Yang Y., Epoxidation of trans-stilbene and cis-cyclooctene over mesoporous vanadium catalysts: Support composition and pore structure effect. *Appl. Catal. A*, **419:**194 (2012).

[35] Brydon R. R., Peng A., Qian L., Kung H. H., Broadbelt L. J., Microkinetic modeling of homogeneous and gold nanoparticle-catalyzed oxidation of cyclooctene. *Ind. Eng. Chem. Res.,* **57**:4832 (2018).

[36] Adam M. S. S., Hafez A. M., El-Ghamry I. Catalytic performance of binary and ternary oxovanadium complexes of dipyridinyl-urea in (ep) oxidation of cis-cyclooctene and 1-octene. *Reac. Kinet. Mech. Catal.*, **124**:779 (2018).

[37] Skliri E., Papadogiorgakis S., Lykakis I. N., Armatas G. S., Mesoporous assembled Mn3O4 nanoparticle networks as efficient catalysts for selective oxidation of alkenes and aryl alkanes. *Chem. Plus. Chem*, **82**:136 (2017).