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FULL PAPER

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Post modification of zinc based coordination polymer to prepare Zn-Mo-ICP nanoparticles as efficient self-supported catalyst for olefin epoxidation

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Preparation, characterization, and catalytic properties of bimetallic coordination polymer constructed from 2-aminoterephthalic acid as linker, zinc cations as node, and cis-dioxo molybdenum units as catalytic active sites are reported via two pathways. Molybdenum centers were placed in N,O positions created by condensation reaction of 2-aminoterephthalic acid with salicylaldehyde while zinc cations coordinated via carboxylic acid groups of linker to achieve infinite chains of metalo-ligand. The obtained coordination polymer was fully characterized and its catalytic properties in the epoxidation of olefins with tert-butyl hydroperoxide (TBHP) described. In comparison with previously reported heterogenized molybdenum catalysts, this new coordination polymer exhibited good conversion as well as high selectivity in the epoxidation of olefins. The catalyst is stable under ambient conditions and could be reused as active catalyst for at least five times.

KEYWORDS
bi-metallic coordination polymer, epoxidation, heterogeneous catalyst, nanoparticles

1 | INTRODUCTION

Physical properties and size distribution of catalysts are two important features that affect their activities and recoverabilities in catalytic reactions.[1] For nanosized heterogeneous catalysts it is important to hold reactivity and stereoselectivity in chemical transformations.[2–4] A number of methods have been developed to heterogenize or immobilize the homogeneous catalysts on solid materials.[5–10] A promising method involves heterogenization of the precursor by ligand modification to prepare self-supporting insoluble polymeric network architecture.[11] In comparison, the self-supporting method produces heterogeneous catalysts with high density of catalytically active centers via the immobilization process.

Infinite coordination polymers (ICPs) as new class of coordination polymers are prepared via preventing crystal growth at the nano- or micro-size stage through solvent-induced precipitation.[12–15] The resulting ICP particles have typically amorphous, rather than crystalline structures. These compounds have several applications in gas storage,[16–20] mixture separations,[21,22] antisense gene regulation,[23] optoelectronics,[24] and drug delivery.[25,26] Many crystalline metal–organic framework catalysts are reported,[27–30] but few utilization of nano/micro infinite coordination polymers as catalysts has been described.[2,31,32]

Sweigart and his coworkers reported the preparation and catalytic activity of the self-supported organometallic rhodium quinonoid nanocatalyst which showed high activity in the stereoselective polymerization of phenylacetylene.[2] Feng prepared hollow-shell microspheres of Zr-based coordination polymer using MnO_2 microspheres as template for immobilizing enzyme catalysts with high efficiency for oxidase- and catalase-like activities.[33] The use of zinc based ICP particles as an effective heterogeneous catalyst for Michael addition of 1-methylpyrrole to benzylideneacetone and β-nitrostyrene was demonstrated by Morsali.[34] Tang reported a redox and catalytically active 'all-in-one' infinite coordination polymer to achieve electrochemical immunosensor for detection of low-abundance protein (Prostate-specific antigen as a model).[35] Fu synthesized flower-like microparticles of Ni-Co/BDC and Co/BDC (BDC = 1,4-benzenedicarboxylate) catalyst for cycloaddition of CO_2 to phenyl epoxide which completely produced phenyl cyclic carbonates with high yields.[36]

Herein, we report the synthesis of zinc based infinite coordination polymer by coordination-polymerization of 2-aminoterephtalic acid and zinc cation. Post modification of the prepared **Zn-ICP** gives a suitable N,O coordination position for stabilizing molybdenum center and preparation of new heterogenized molybdenum catalyst (**Zn-Mo-ICP**; path-1). This catalyst can be obtained from another pathway; path-2, Schiff base condensation of the amine group of 2-aminoterephthalic acid with salicylaldehyde give new N,O position for coordinating to molybdenum center. The obtained metalo-ligand unit can be polymerized via coordination-polymerization with zinc cation. The catalytic activity of the prepared **Zn-Mo-ICP** catalyst is studied which shows good conversion and selectivity in the epoxidation of olefins with tert-butylhydroperoxide.

2 | EXPERIMENTAL

The details of used materials and instrumentations have been included in supplementary information. Bis (acetylacetonato) dioxo molybdenum (VI) was prepared according to previous report.[37]

Scheme 1 shows step by step preparation of **Zn-Mo-ICP** via two different paths.

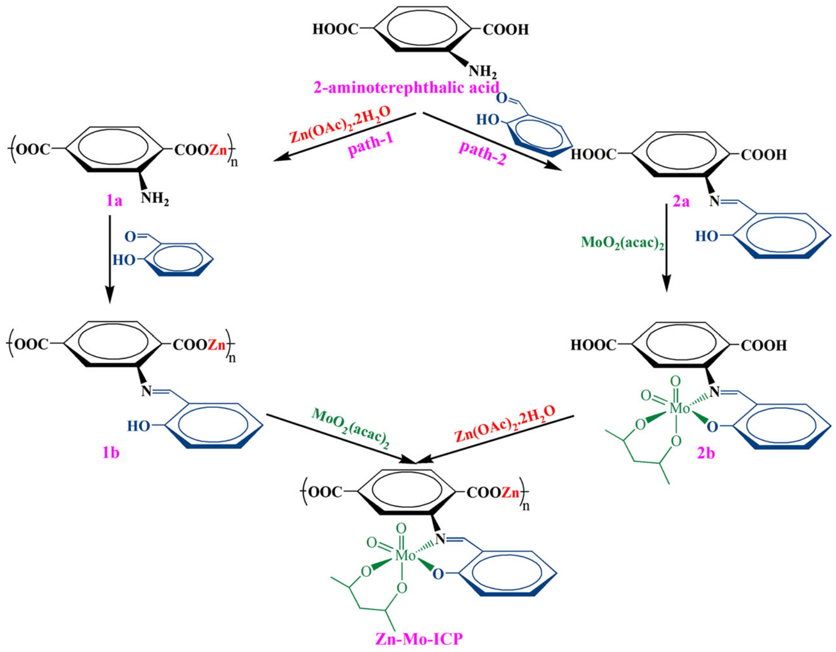
2.1 | Synthesis of Zn-Mo-ICP through path-1

2.1.1 | Synthesis of 1a

0.7 g (3.86 mmol) of 2-aminoterephthalic acid was dissolved in 40 m hot methanol, and 10 mL methanolic solution of Zn $(OAc)_2.2H_2O$ (1.27 g; 5.80 mmol) was added to above solution slowly. Fine yellow crystals of the product were formed spontaneously and the reaction mixture stirred for 15 min. Afterwards, the product was isolated, and subsequently washed with methanol several times via centrifugation–redispersion cycles. Each successive supernatant was decanted and replaced with fresh methanol. The product was collected and dried under vacuum (0.90 g; 97% yield).

2.1.2 | Synthesis of 1b

0.75 g (6.17 mmol) of salicylaldehyde in 10 ml MeOH was added to 30 ml methanolic dispersion of 0.25 g (1.03 mmol) **Zn-ICP** (**1a**) and the resulting mixture refluxed for 24 hr. The product was filtered, soxhlet washed with methanol for 24 hr to remove unreacted



SCHEME 1 Illustrative preparation steps of the **Zn-Mo-ICP** through two paths.

salicylaldehyde, and finally dried under vacuum (0.31 g; 87% yield).

2.1.3 | Synthesis of Zn-Mo-ICP (I)

Warm THF solution of $MoO_2(acac)_2$ (0.67 g; 2.05 mmol; 20 ml) was added to a dispersed mixture of 0.23 g (0.66 mmol) **1b** in 20 ml THF. The resulting mixture was refluxed for 24 h, isolated by centrifugation, and soxhlet washed with THF for 24 hr. The obtained product was dried under vacuum (0.25 g; 66% yield).

2.2 | Synthesis of Zn-Mo-ICP through path-2

2.2.1 | Synthesis of 2a

Excess amount of salicylaldehyde (1.89 g; 15.4 mmol) in 20 ml MeOH was added to 30 ml methanolic solution of 2-aminoterephtalic acid (0.7 g; 3.86 mmol). The color of solution changed to deep orange immediately. After refluxing for 24 hr, the solution was evaporated and the orange solid precipitate was separated and soxhlet washed with $CHCl_3$ for 24 hr to fully remove unreacted salicylaldehyde. The product was dried under vacuum (0.8 g; 73% yield).

2.2.2 | Synthesis of 2b

20 ml THF solution of $MoO_2(acac)_2$ (1.44 g; 4.42 mmol) was added to a solution of **2a** (0.42 g; 1.47 mmol) in 30 ml THF. The solution was refluxed for 24 hr and the precipitate was soxhlet washed for 24 hr with $CHCl_3$ to remove unreacted $MoO_2(acac)_2$ and finally dried under vacuum (0.38 g; 50% yield).

2.2.3 | Synthesis of Zn-Mo-ICP (II)

0.37 g (0.72 mmol) of complex **2b** was dissolved in 30 ml MeOH, and 20 ml solution of 0.31 g (1.45 mmol) $Zn(OAc)_2.2H_2O$ in MeOH was added. The spontaneously formed green precipitate was stirred for one hour. The precipitate was isolated and washed with hot MeOH via centrifugation-redispersion cycles and vacuum dried (0.348 g; 84% yield).

2.3 | Investigation of catalytic activity of Zn-Mo-ICP in the epoxidation of olefins

Epoxidation of olefins with tert-butylhydroperoxide (80% in di-tertiary butyl peroxide, TBHP) as oxidant was carried out in a round bottomed flask equipped with a condenser and magnetic stirrer under nitrogen atmosphere. The catalyst was activated at 70 °C in vacuum oven overnight before every use. In a typical procedure, TBHP (7.2 mmol) was added to a mixture of olefin (4 mmol) and catalyst (50 mg) in chloroform (5 ml) and the reaction mixture refluxed under nitrogen atmosphere. Samples were withdrawn in specific times and analyzed by gas chromatography. Recovery test was performed as follow: the used catalyst was collected and soxhlet washed with chloroform for 24 hr and then reused in cyclooctene epoxidation under above-mentioned conditions. The molybdenum content of recycled catalyst was measured with inductively coupled plasma-optical emission spectroscopy (ICP-OES). Investigation of homogeneous or heterogeneous nature of the catalytic reaction was also checked. For this propose, the epoxidation of cyclooctene was allowed to proceed 2 hr and the catalyst then filtered at the reaction temperature. The solution was transferred into a clean flask and refluxed for 22 hr. The conversion and selectivity were determined after 2 and 24 hr. The molybdenum content of recycled catalyst was also measured with ICP-OES that found to be about 15.04 wt%.

3 | RESULTS AND DISCUSSION

The bi-metallic coordination polymer, **Zn-Mo-ICP**, was prepared through two pathways (Scheme 1). In path-1, **Zn-ICP** (**1a**) was prepared via coordination-polymerization of 2-aminoterephtalic acid as linker and Zn^{2+} as node. Next, amine group of **1a** produced imine bond via Schiff base condensation with salicylaldehyde to form **1b**. Finally, the reaction of **1b** with $MoO_2(acac)_2$ produced **Zn-Mo-ICP (I)** via replacing one of the acetylacetonate groups.

In path-2, first condensation reaction of 2-aminoterephtalic acid with salicylaldehyde gave **2a** with two coordination positions i.e. N,O and COO. The prepared ligand, **2a,** was reacted with $MoO_2(acac)_2$ to form **2b** in which Mo located at N,O position. Coordination-polymerization of **2b** in the presence of Zn^{2+} achieved desired product, **Zn-Mo-ICP (II)** in which carboxylate positions connected to each other via Zn^{2+} nodes. The results of C, H, N, Zn, and Mo elemental analysis entirely confirmed the formation of desired products in each step (Table 1).

TABLE 1 C, H, N, Mo, and Zn elemental analysis results of the precursors and products

	C Found (Calc.)	H Found (Calc.)	N Found (Calc.)	Zn Found (Calc.)	Mo Found (Calc.)
1a ($C_8H_5NO_4Zn.1.5H_2O$)	35.75 (35.39)	2.87 (2.97)	4.95 (5.16)	24.37 (24.08)	–
1b ($C_{15}H_9NO_5Zn.1.5H_2O$)	47.73 (47.96)	3.39 (3.22)	3.95 (3.73)	17.03 (17.40)	–
Zn-Mo-ICP (I) ($C_{20}H_{15}NO_9MoZn.1.5H_2O$)	40.05 (39.92)	3.27 (3.02)	2.19 (2.33)	10.52 (10.87)	15.61 (15.95)
2a ($C_{15}H_{11}NO_5$)	63.34 (63.16)	3.51 (3.89)	4.61 (4.91)	–	–
2b ($C_{20}H_{17}NO_9Mo.2H_2O$)	43.51 (43.89)	3.49 (3.87)	2.67 (2.56)	–	17.23 (17.53)
Zn-Mo-ICP (II) ($C_{20}H_{15}NO_9MoZn.2H_2O$)	39.65 (39.34)	3.39 (3.14)	2.45 (2.29)	10.32 (10.71)	15.34 (15.71)

To further approve the elemental composition of **Zn-Mo-ICP (I)** and **(II)**, the products were analyzed by energy dispersive X-ray (EDX) spectroscopy (Figure 1). It can be deduced from EDX spectra that both of the products have the same composition of C, N, O, Zn, and Mo elements.

For monitoring the functionalization steps, FT-IR spectra of the precursors and the obtained products by

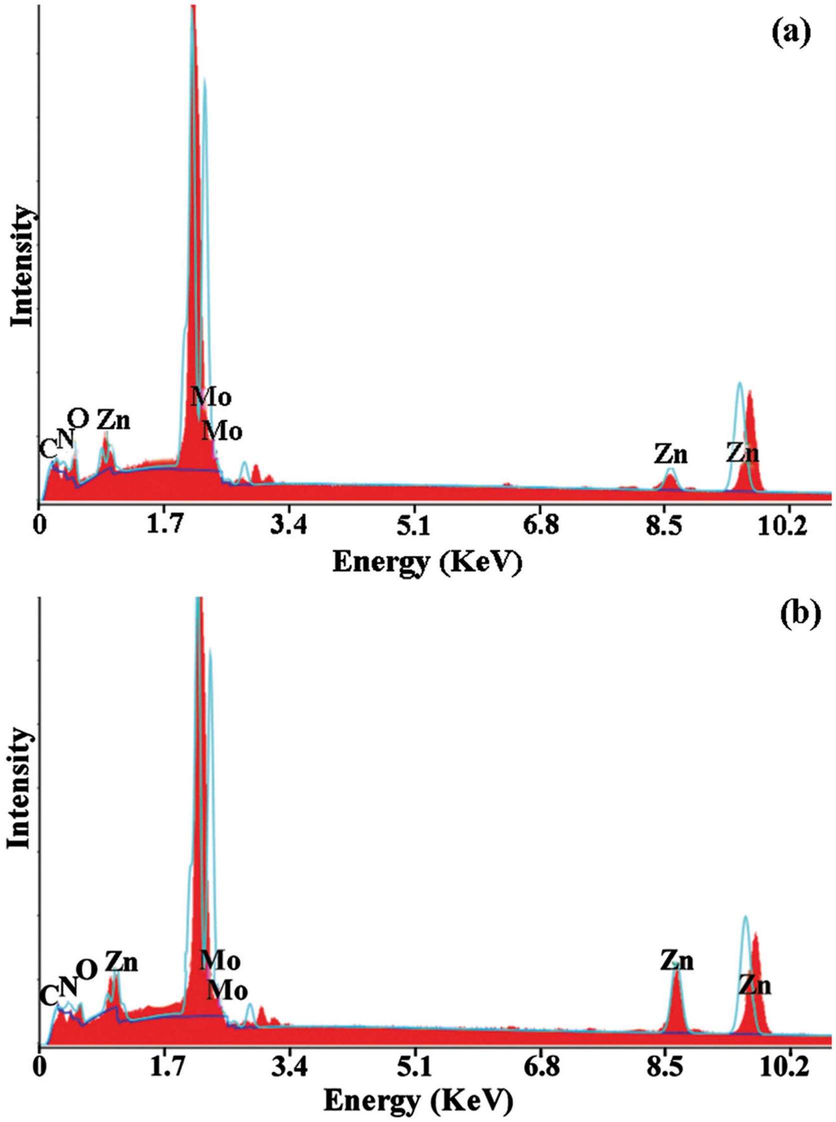


FIGURE 1 EDX spectra of a) **Zn-Mo-ICP (I)** and b) **Zn-Mo-ICP (II)**

path-1 and path-2 were acquired and shown in Figure 2. As seen in path-1 (Figure 2a), by coordinating carboxylate groups of 2-aminoterephtalic acid to Zn^{2+}, the COOH frequency at 1687 cm^{-1} was shifted to 1561 cm^{-1} confirming the formation of **Zn-ICP**, **1a**. Comparison of the FT-IR spectra of **1a** and **1b** shows the disappearance of amine stretching vibrations at 3472 and 3332 cm^{-1} in **1a** and appearance of imine band at 1626 cm^{-1} in **1b**. After formation of **Zn-Mo-ICP (I)**, the imine band shifts to lower frequency from 1626 cm^{-1} to 1603 cm^{-1} due to the coordination of N,O site of the ligand to Mo center. The presence of two new peaks at 934 and 905 cm^{-1} attributed to *cis*-MoO_2 stretching vibrations confirmed the presence of molybdenum complex in **Zn-Mo-ICP (I)**.

In path-2 (Figure 2b), two peaks of 2-aminoterephtalic acid at 3505 and 3392 cm^{-1} assigned to the N-H stretching vibrations were disappeared by reaction with salicylaldehyde and formation of imine bond whose stretching vibration appeared at 1614 cm^{-1}. The shift of imine band from 1614 cm^{-1} to 1605 cm^{-1} and appearance of *cis*-MoO_2 stretching frequencies at 947 and 907 cm^{-1} verified the formation of **2b**. Finally, carboxylic acid stretching frequency of **2b** at 1699 cm^{-1} was shifted to 1551 cm^{-1} by coordination to Zn^{2+} and formation of **Zn-Mo-ICP (II)**.

The X-ray diffraction (XRD) patterns of **Zn-Mo-ICP (I)** and **Zn-Mo-ICP (II)** as well as **Zn-ICP** were investigated to more elucidate the structure and crystallinity of the products. The XRD pattern of **Zn-ICP** is somewhat different from **Zn-Mo-ICP** and show more crystallinity. The prepared **Zn-Mo-ICP** products achieved from two different pathways exhibited identical XRD patterns

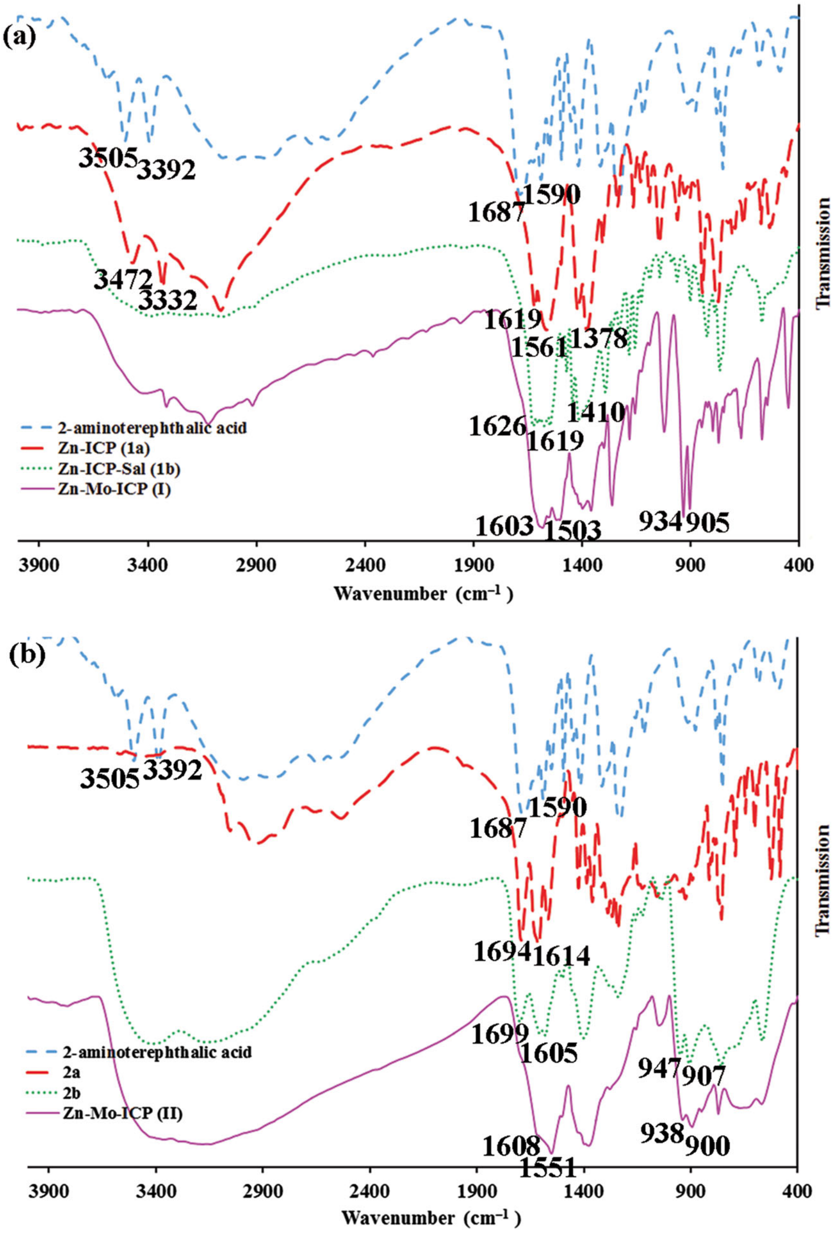


FIGURE 2 FT-IR spectra of step by step formation of a) **Zn-Mo-ICP (I)** and b) **Zn-Mo-ICP (II)**

regardless of their preparation path (Figure 3). Such similarity suggested the identical unit cells for both samples and showed that the reaction path has no effect on the molecular packing arrangement. The XRD patterns also revealed relatively low crystallinity of the products and all attempts to obtain a single crystal suitable for X-ray crystallography analysis were failed.

The room temperature photoluminescence spectra (RT-PL) of the 2-aminoterephthalic acid and corresponding coordination polymers were shown in Figure 4. Upon excitation of 2-aminoterephthalic acid at 365 nm, an emission peak at 565 nm was observed which blue shifted to 430 nm upon coordination to Zn^{2+} (**Zn-ICP**; $\lambda_{ex} = 330$ nm).

Zn-Mo-ICP (I) and **Zn-Mo-ICP (II)** products showed entirely the same PL spectra under excitation at 380 nm. Compared with the free ligand, the observed blue-shift of emission bands implied to coordination of the ligand to the metal ions and formation of coordination polymers.

Based on the above results, **Zn-Mo-ICP (I)** and **Zn-Mo-ICP (II)** have completely the same structures. So, **Zn-Mo-ICP (II)** with higher yield was chosen for further X-ray photoelectron spectroscopy (XPS), TGA analyses, and catalytic studies.

Zn-Mo-ICP (II) was selected to study the composition and chemical states of each element and confirm the proposed structure by XPS. The wide scan XPS spectrum of **Zn-Mo-ICP (II)** (Figure 5) clearly demonstrated the characteristic peaks of molybdenum, carbon, nitrogen, oxygen, and zinc.

A Mo doublet peak is present at the 231.7 and 234.9 eV corresponding to $3d_{5/2}$ and $3d_{3/2}$ Mo (VI), respectively.[38]

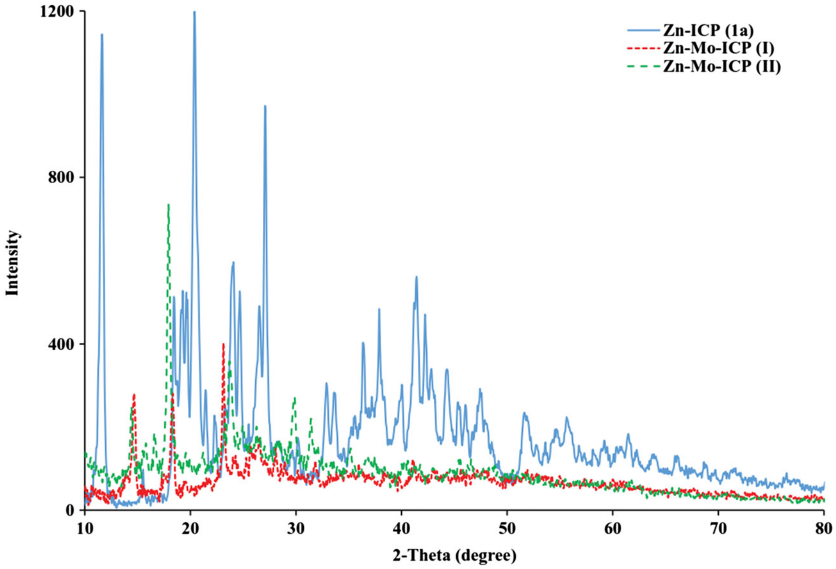


FIGURE 3 XRD patterns of **Zn-ICP**, **Zn-Mo-ICP (I)**, and **Zn-Mo-ICP (II)**

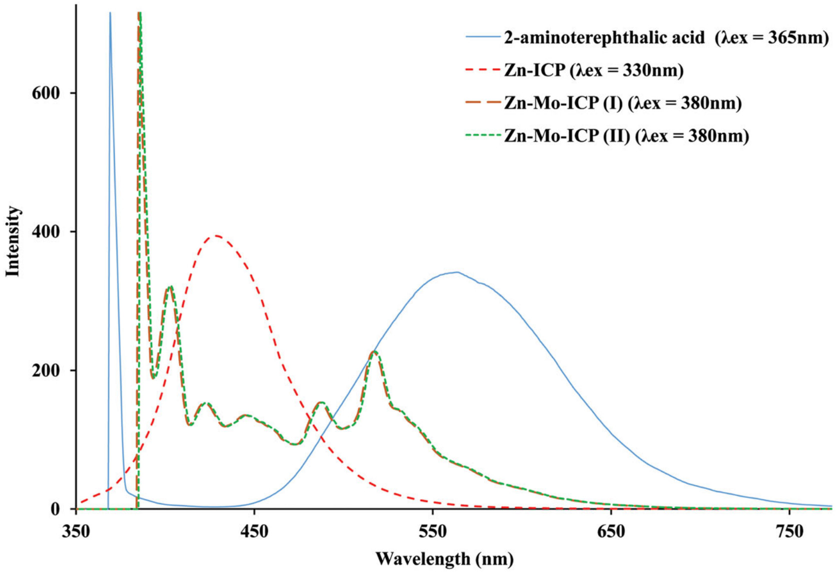


FIGURE 4 RT-PL spectra of 2-aminoterephthalic acid ligand and corresponding coordination polymers

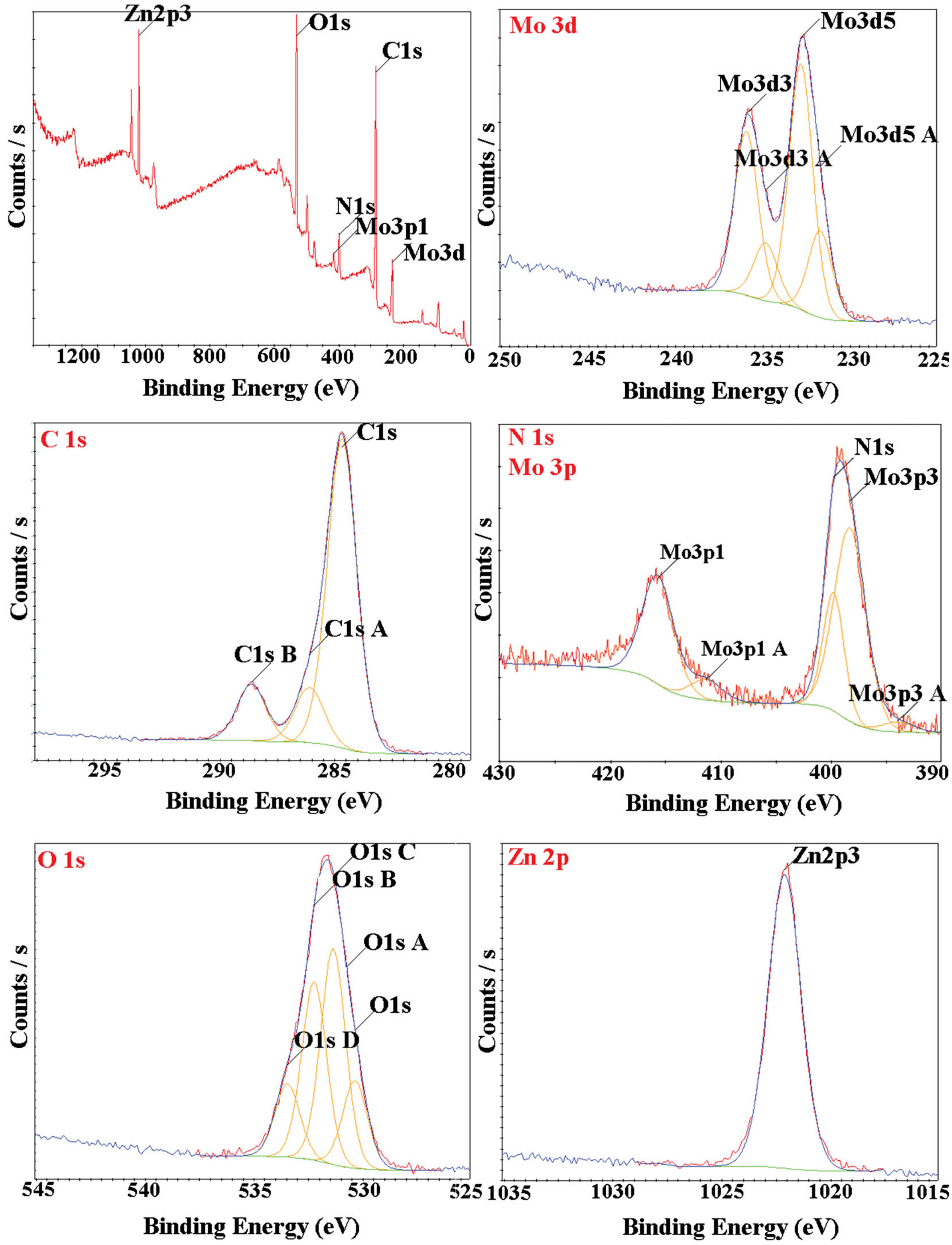


FIGURE 5 XPS wide scan spectrum and high resolution Mo 3d, C 1 s, N 1 s, O 1 s, and Zn 2p deconvoluted spectra of **Zn-Mo-ICP (II)**

The C1s peak can be resolved into two sub-peaks at 286.1 and 288.6 eV corresponding to the presence of carbon in two chemical states i.e. sp^3 in C-C, C-O, C-H, and sp^2 in C=C, C=N and C=O, respectively.[39] Deconvolution of the N 1 s high resolution spectrum illustrates just one peak exactly existed at 399.79 eV owing to the presence of imine nitrogen. The O 1 s spectrum shows four peaks from 530.4 to 533.5 eV due to the presence of oxygen in different chemical environments i.e. C-O-Zn, C-O-Mo, C=O, and Mo = O groups. The observed peak at 1022.1 eV can be attributed to the binding energy of Zn $2p_{3/2}$, indicating the presence of Zn^{2+} in the **Zn-Mo-ICP**. It is worth noting that the signals of Mo 3d, N 1 s and Zn $2p_{3/2}$ after deconvolution of the full XPS spectrum consist of just one component corresponding to one species. Such observations clearly verify the composition and chemical states of all elements in **Zn-Mo-ICP (II)**.

In order to understand the thermal stability of **Zn-Mo-ICP (II)**, thermogravimetric analysis (TGA) was carried out (Figure 6). A small weight loss of about 6.79% was

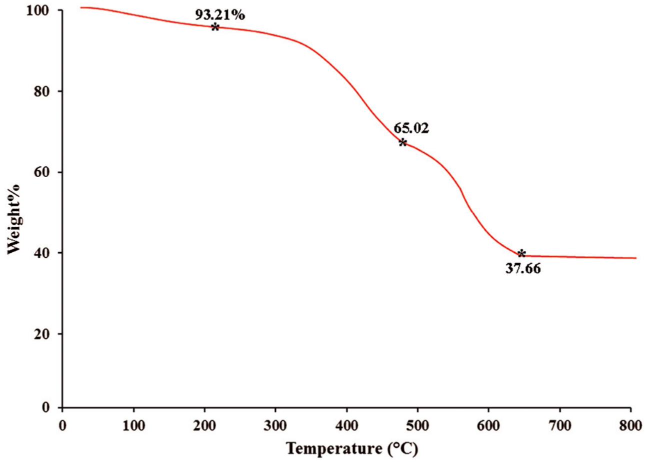


FIGURE 6 TGA curve of **Zn-Mo-ICP (II)** obtained from path-2

observed in the initial stage (< 250 °C), attributed to the presence of two water molecules in the sample (calculated 5.90%). The major weight loss happened at two well-defined steps, one starting at 300 °C and ending at 490 °C (with 28.19% weight loss) and the other from 490 °C to 650 °C (with 27.36% weight loss) attributed to organic ligand decomposition. The final residual weight is 37.66% corresponding to MoO_3 + ZnO (calculated 36.90). Based on the CHN, ICP-OES, and TGA analyses, $C_{20}H_{15}NO_9MoZn.2H_2O$ chemical formula was deduced for **Zn-Mo-ICP (II).**

Figure 7 shows scanning electron microscopy (SEM) images of the **Zn-ICP** and **Zn-Mo-ICP** products prepared from two pathways. The images revealed that **Zn-ICP** (Figure 7a) includes monodispersed nanoparticles with average diameter of 50 nm, while two different morphologies are seen for **Zn-Mo-ICP** products obtained from two pathways. **Zn-Mo-ICP (I)** showed no well-defined morphology. Figure 7b shows microstructures containing some nanoparticles with average diameter of about 40 nm (Figure 7b). However, the **Zn-Mo-ICP (II)** is mainly consisted of microparticles formed from intertwining of nanoplates (Figure 7c). Figure 7d displays the high magnification image of several microparticles of **Zn-Mo-ICP (II)** with 200–250 nm diameter assembled from nanoplates with smooth surface. These nanoplates have 300 nm diameter and very thin thickness (25 nm), which fit the characteristics of 2D materials. The thickness distribution was averaged by counting 40 nanoplates which showed the thickness of nanoplates distributed from 20 nm to 35 nm,

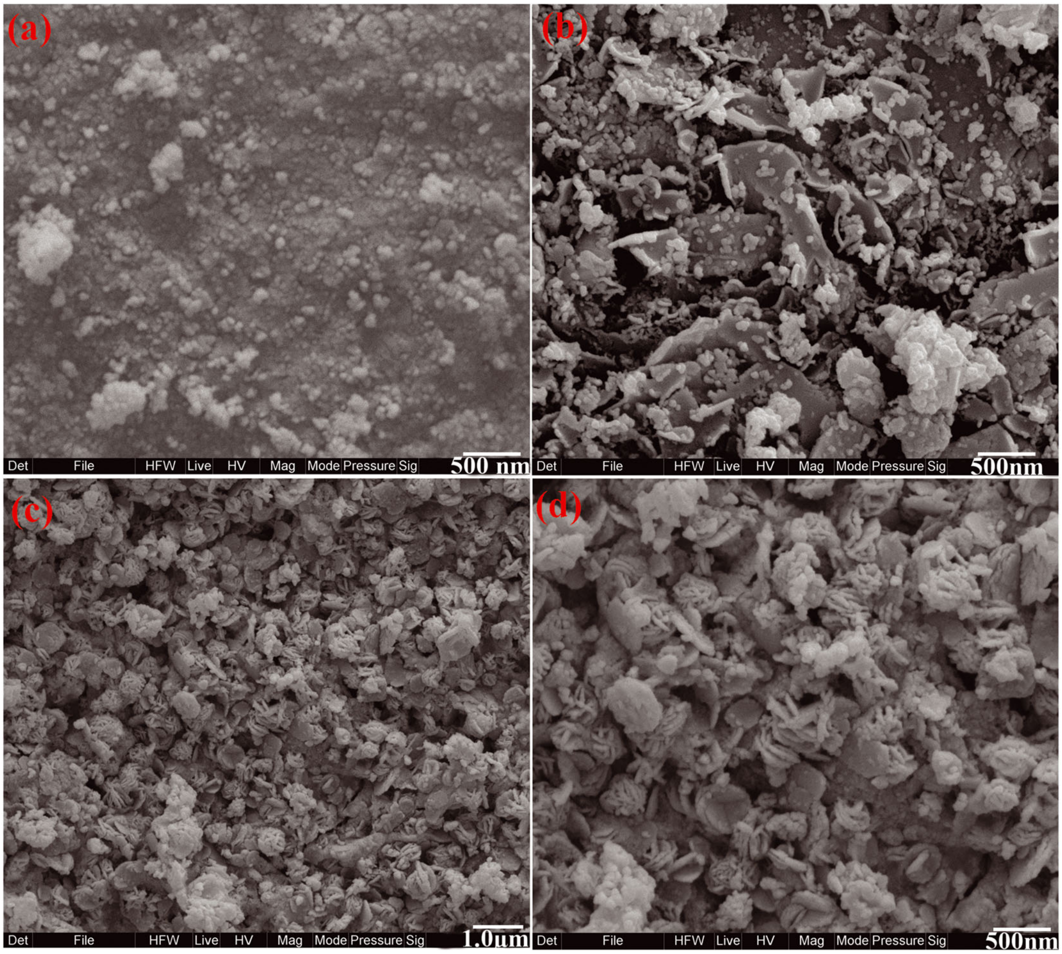


FIGURE 7 SEM images of a) **Zn-ICP,** b) **Zn-Mo-ICP (I**), and c, d) **Zn-Mo-ICP (II)**

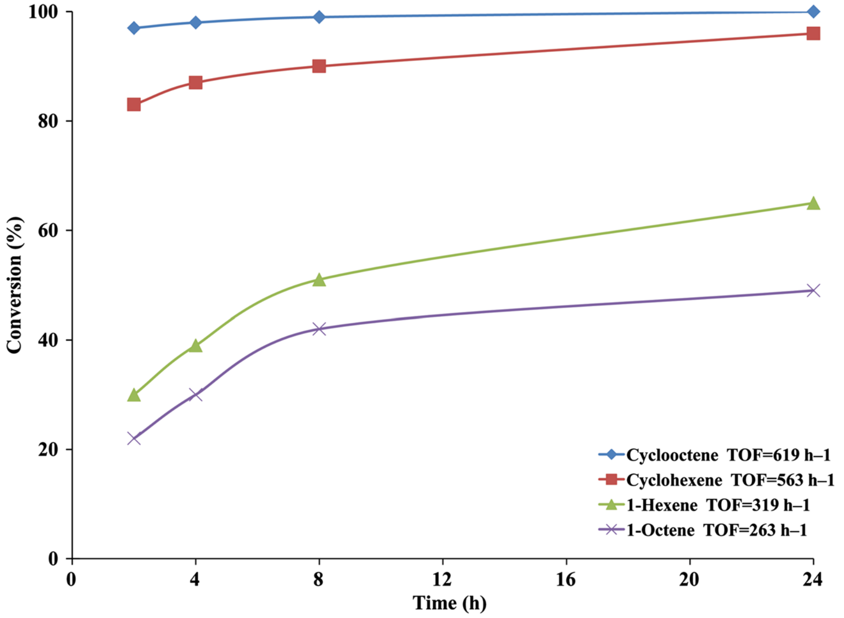


FIGURE 8 Results of olefin epoxidation with TBHP in the presence of **Zn-Mo-ICP (II)**. Reaction conditions: catalyst (50 mg), olefin (4 mmol), TBHP (7.2 mmol), refluxing chloroform (5 ml). TOF values are calculated as mmol of product formed per mmol of molybdenum in the catalyst per hour

TABLE 2 Camparison of some of the previous works with current

Catalyst	Time (h)	Solvent		Conversion (%)	Selectivity (%)[a]	Reference
Zn-Mo-ICP	8	$CHCl_3$	TBHP	93	> 99	This work
$[Mo(O)(O_2)_2L]$	18	$CHCl_3$	H_2O_2	2–99	-	[47]
MoO_2-L-MCM41	9	$CHCl_3$	TBHP	35–99	99	[44]
MoO_2-chitosan-Fe_3O_4	8	$CHCl_3$	TBHP	99–100	99	[48]

and the average value was calculated to be 25 nm. TEM image of **Zn-Mo-ICP (II)** is shown in Figure S1.

The **Zn-Mo-ICP (II)** was exploited in catalytic epoxidation of olefins with TBHP as oxidant. The results in Figure 8 show that the olefins are converted selectively (>99%) to their corresponding epoxides. Inspection of the results reveals that the catalytic activity is olefin dependent with cyclic olefins displaying higher conversions. The sequence of increasing reactivities based on the turnover frequencies (TOFs) is:

cyclooctene > cyclohexene >1-hexene >1-octene.

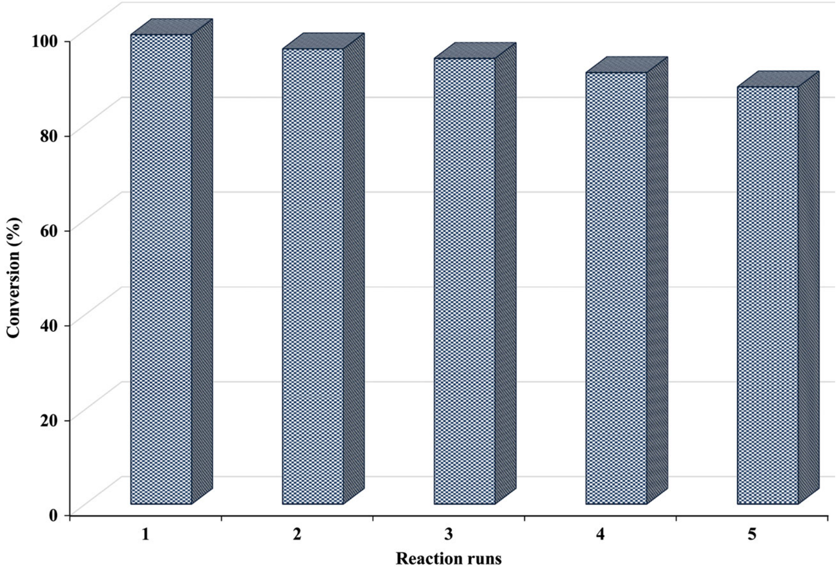


FIGURE 9 Results of cyclooctene epoxidation with TBHP in the presence of recycled **Zn-Mo-ICP (II)** after 8 hr

TABLE 3 Results of the cyclooctene epoxidation with TBHP in different conditions

Catalyst	Time (h)	Conversion (%)	Selectivity (%)[a]
–	12	14	41
Zn-ICP	12	17	36
Zn-Mo-ICP	2	85	> 99
After filtering the catalyst	22	87	> 99

Reaction conditions: catalyst (50 mg), olefin (4 mmol), TBHP (7.2 mmol), refluxing chloroform (5 ml).

[a] Selectivity toward epoxycyclooctene.

To investigate this trend, two main factors i.e. electronic and steric effects should be taken into account. As reported earlier,[40] mechanism of olefin epoxidation with molybdenum catalysts involves the nucleophilic attack of olefin C=C double bond to electron deficient peroxidic oxygen of coordinated TBHP. Thus, cyclic olefins with higher electron density on the C=C double bond have higher tendency for participating in the epoxidation reaction. Due to the presence of more electron donating group in cyclooctene, its reactivity is higher than cyclohexene. On the other hand, 1-octene shows lower reactivity in comparison with 1-hexene as the larger alkyl group connected to its C=C double bond sterically hinders it from closing to the active site of catalyst.

There are several reports in the literature showing satisfactory results of olefin oxidation using a wide variety of catalysts/oxidants,[41–44] which some of them reported in Table 2 with relativity high activity. However, to the best of our knowledge, no reports have been made so far representing oxidation of olefin in the presence of ICP type catalyst with excellent selectivity. Synthesis of 2-D cobalt based MOF and its catalytic activity towards the oxidation of 1-hexene to form oxygenated compounds in the presence of TBHP under solvent free condition was reported by Bora.[45] Catalytic results showed conversion of the starting material to oxygenated products such as 1,2-epoxyhexane, 1-hexanal and a little amount of hexanoic acid, so selectivity for one product did not seen. Two 3D Co-based MOF were prepared by Zhang group and evaluated for catalytic oxidation of cyclooctene.[46] The products of the catalytic reaction were epoxycyclooctane, 1,2-cyclooctanediol and cycloocten-2-one. Against these reports, prepared **Zn-Mo-ICP** in our work shows 100% selectivity for epoxidizing the olefins and the conversions increased with increasing the reaction time.

In order to investigate the reusability of the **Zn-Mo-ICP (II)** as catalyst, at the end of cyclooctene epoxidation, the recovered catalyst was washed and characterized with XRD and FT-IR techniques (Figure S2 and S3). Reusing the recovered catalyst in the cyclooctene epoxidation (Figure 9) showed that it can be recovered five times with permanent conversion of cyclooctene (88–99%) to corresponding epoxide after 8 hr.

To illustrate the critical role of the **Zn-Mo-ICP** catalyst, two separate tests were carried out in the absence of the catalyst (blank) and in the presence of **Zn-ICP** (Table 3). The low conversion of cyclooctene in the absence of the catalyst obviously confirms its critical role in the epoxidation reaction.

Furthermore, to reveal whether the catalysis is occurred in homogeneous or heterogeneous phase, in a separate test, a hot filtration was done 2 hr after starting the reaction. The filtrate was taken back to a clear flask and reaction was continued for 22 hr. It was found that the cyclooctene epoxidation is nearly stopped after separation of the catalyst from the reaction mixture (Table 3). The results confirmed that the catalytic process in the presence of **Zn-Mo-ICP (II)** is truly heterogeneous and any contribution from the solubilized molybdenum species is ruled out.

4 | CONCLUSION

Hybrid molybdenum-zinc based coordination polymer prepared by coordination-polymerization of 2-aminoterephthalic acid showed high activity as heterogeneous catalyst for the selective epoxidation of olefins with TBHP as oxidant under mild conditions. The catalytic performance of this coordination polymer is olefin-dependent and relatively high catalytic activity and selectivity were obtained in $CHCl_3$. The prepared catalyst can be readily recovered and reused for olefin epoxidation for up to five times without loss of activity and selectivity.

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DATA AVAILABILITY

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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REFERENCES

[1] M. Salavati-Niasari, F. Soofivand, A. Sobhani-Nasab, M. Shakouri-Arani, A. Y. Faal, S. Bagheri, *Adv. Powder Technol.* **2016**, *27*, 2066.

[2] K. H. Park, K. Jang, S. U. Son, D. A. Sweigart, *J. Am. Chem. Soc.* **2006**, *128*, 8740.

[3] S. Caron, R. W. Dugger, S. G. Ruggeri, J. A. Ragan, D. H. B. Ripin, *Chem. Rev.* **2006**, *106*, 2943.

[4] M. Salavati-Niasari, Z. Salimi, M. Bazarganipour, F. Davar, *Inorg. Chim. Acta* **2009**, *362*, 3715.

[5] Y. Chang, Y. Lv, F. Lu, F. Zha, Z. Lei, *J. Mol. Catal. A: Chem.* **2010**, *320*, 56.

[6] S. Sharma, S. Sinha, S. Chand, *Ind. Eng. Chem. Res.* **2012**, *51*, 8806.

[7] M. Salavati-Niasari, F. Farzaneh, M. Ghandi, *J. Mol. Catal. A: Chem.* **2002**, *186*, 101.

[8] M. Salavati-Niasari, P. Salemi, F. Davar, *J. Mol. Catal. A: Chem.* **2005**, *238*, 215.

[9] M. Niakan, Z. Asadi, M. Masteri-Farahani, *Appl. Surf. Sci.* **2019**, *481*, 394.

[10] M. Masteri-Farahani, P. Eghbali, E. Şahin, *Colloids Surf. A Physicochem. Eng. Asp.* **2019**, *570*, 347.

[11] D. Habibi, A. Faraji, M. Arshadi, J. Fierro, *J. Mol. Catal. A: Chem.* **2013**, *372*, 90.

[12] C. A. M. Moonhyun Oh, *Nature* **2005**, *438*, 651.

[13] W. Cho, S. Park, M. Oh, *Chem. Commun.* **2011**, *47*, 4138.

[14] S.-j. Park, W. Cho, M. Oh, *CrstEngComm* **2010**, *12*, 1060.

[15] D. K. Alexander, M. Spokoyny, A. Sumrein, C. A. Mirkin, *Chem. Soc. Rev.* **2009**, *38*, 1218.

[16] A. M. S. Omar, K. Farha, K. L. Mulfort, S. Galli, J. T. Hupp, C. A. Mirkin, *Small* **2009**, *5*, 1727.

[17] K. L. Mulfort, J. T. Hupp, *J. Am. Chem. Soc.* **2007**, *129*, 9604.

[18] O. K. Farha, A. M. Spokoyny, K. L. Mulfort, M. F. Hawthorne, C. A. Mirkin, J. T. Hupp, *J. Am. Chem. Soc.* **2007**, *129*, 12680.

[19] M. Dinca, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann, J. R. Long, *J. Am. Chem. Soc.* **2006**, *128*, 16876.

[20] K. L. Mulfort, J. T. Hupp, *Inorg. Chem.* **2008**, *47*, 7936.

[21] Y.-S. Bae, K. L. Mulfort, H. Frost, P. Ryan, S. Punnathanam, L. J. Broadbelt, J. T. Hupp, R. Q. Snurr, *Langmuir* **2008**, *24*, 8592.

[22] Y.-S. Bae, O. K. Farha, A. M. Spokoyny, C. A. Mirkin, J. T. Hupp, R. Q. Snurr, *Chem. Commun.* **2008**, 4135.

[23] C. M. Calabrese, T. J. Merkel, W. E. Briley, P. S. Randeria, S. P. Narayan, J. L. Rouge, D. A. Walker, A. W. Scott, C. A. Mirkin, *Angewandte Chemie* **2015**, *127*, 486.

[24] M. Alvaro, E. Carbonell, B. Ferrer, F. X. Llabrés i Xamena, H. Garcia, *Chem. A Eur. J.* **2007**, *13*, 5106.

[25] P. Horcajada, C. Serre, M. Vallet-Regí, M. Sebban, F. Taulelle, G. Férey, *Angewandte Chemie* **2006**, *118*, 6120.

[26] S. M. Cohen, *Curr. Opin. Chem. Biol.* **2007**, *11*, 115.

[27] H. Zhang, M. Oh, C. Allen, E. Kumacheva, *Biomacromolecules* **2004**, *5*, 2461.

[28] S.-H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp, T. E. Albrecht-Schmitt, *Chem Comm* **2006**, 2563.

[29] S. J. Titinchi, H. S. Abbo, *Catal. Today* **2013**, *204*, 114.

[30] P. G. Cozzi, *Chem. Soc. Rev.* **2004**, *33*, 410.

[31] W. Xie, J. Wang, *Biomass Bioenergy* **2012**, *36*, 373.

[32] R. K. Sharma, Y. Monga, A. Puri, G. Gaba, *Green Chem.* **2013**, *15*, 2800.

[33] J. Sun, Y. Fu, R. Li, W. Feng, *Chem. Mater.* **2018**, *30*, 1625.

[34] R. Nouri, S. Abedi, A. Morsali, *J. Iran. Chem. Soc.* **2017**, *14*, 1601.

[35] B. Zhang, B. Liu, G. Chen, D. Tang, *Biosens. Bioelectron.* **2015**, *64*, 6.

[36] W.-Z. Li, Y. Zhou, F. Liu, Y. Li, M.-J. Xia, E.-H. Han, T. Wang, X. Zhang, Y. Fu, *Nanomaterials* **2017**, *7*, 237.

[37] G. J. Chen, J. W. McDonald, W. Newton, *Inorg. Chem.* **1976**, *15*, 2612.

[38] A. J. Pardey, N. Manosalva, M. Bartolini, J. Molina, M. C. Ortega, L. D'Ornelas, C. Chinea, C. Scott, P. Betancourt, C. Urbina, *Catal. Lett.* **2008**, *122*, 274.

[39] A. A. Qaiser, M. M. Hyland, *Mater. Sci. Forum, Trans. Tech. Publ.* **2010**, *657*, 35.

[40] M. Masteri-Farahani, N. Tayyebi, *J. Mol. Catal. A: Chem.* **2011**, *348*, 83.

[41] H. Alshammari, P. J. Miedziak, S. Bawaked, D. W. Knight, G. J. Hutchings, *ChemCatChem* **2012**, *4*, 1565.

[42] S. Song, P. Wang, Y. He, J. Li, M. Dong, J. Wang, T. Tatsumi, W. Fan, *Microporous Mesoporous Mater.* **2012**, *159*, 74.

[43] A. A. A. Aziz, *J. Mol. Struct.* **2010**, *979*, 77.

[44] M. Masteri-Farahani, *J. Mol. Catal. A: Chem.* **2009**, *316*, 45.

[45] S. J. Bora, R. Paul, M. Nandi, P. K. Bhattacharyya, *J. Solid State Chem.* **2017**, *256*, 38.

[46] G. Zhang, Y. Shi, Y. Wei, Q. Zhang, K. Cai, *Inorg. Chem. Commun.* **2017**, *86*, 112.

[47] M. Herbert, F. Montilla, A. Galindo, *J. Mol. Catal. A: Chem.* **2011**, *338*, 111.

[48] M. Mohammadikish, S. H. Hashemi, *J. Mater. Sci.* **2019**, *54*, 6164.

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