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Manganese and cobalt-terephthalate metal-organic frameworks as a precursor for synthesis of  $Mn_2O_3$ ,  $Mn_3O_4$  and  $Co_3O_4$  nanoparticles: Active catalysts for olefin heterogeneous oxidation

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#### Manganese and Cobalt-terephthalate Metal-Organic Frameworks as a Precursor for Synthesis of Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub> Nanoparticles: Active Catalysts for Olefin Heterogeneous Oxidation

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The thermal decomposition of manganese and cobalt-terephthalate Metal-Organic Framework precursors was utilized as a synthetic route for fabrication of  $Co_3O_4$ ,  $Mn_3O_4$  and  $Mn_2O_3$  nanoparticles. The prepared metal oxide nanoparticles of  $Co_3O_4$ ,  $Mn_3O_4$  and  $Mn_2O_3$  possess average size diameter of 40, 60 and 80 nm respectively. The findings demonstrate that spinel structure nanoparticles of  $Co_3O_4$  and  $Mn_3O_4$  exhibit efficient catalytic activity toward heterogeneous olefin epoxidation in the presence of *tert*-butyl hydroperoxide. In addition,  $Co_3O_4$  and  $Mn_3O_4$  nanoparticles illustrated excellent catalytic stability and reusability for nine and four cycles, respectively, towards olefin oxidation.

Keywords: metal-oxide nanoparticles, epoxidation reaction, heterogeneous catalyst, recyclable catalyst.

Nanoscale materials, including nanoparticles (NPs), nanowires, nanorods, nanotubes and nanoribbons, represent highly customizable and robust multifunctional platforms in many fields. Nanoscale materials behaviors strongly depend on the shape and size of the particles [1]. Among wide variety of transition metal oxides, NPs,  $Co_3O_4$  and  $Mn_3O_4$  are important oxides with spinel structure comprising  $M^{2+}$  and  $M^{3+}$  ions. Chemical and thermodynamical stability of

cobalt and manganese oxides make them promising materials that have received widespread attention due to their appealing multi-functional properties of technological interest [2].

A wide range of synthetic techniques has been applied to grow cobalt and manganese oxide nanosystems with controlled properties, for instance, hydrothermal route using hydrogen peroxide [3], microwave-assisted synthesis via urea hydrolysis [4], hydrothermal process [5], solvothermal method [6], CTAB-assisted solvothermal method [7], microwave-assisted solvothermal method [8], micelle-assisted hydrothermal method [9] and microemulsion-based method [10]. Among these synthetic routes, Metal-Organic Frameworks (MOFs) are favorable for the formation of uniformly separated micrometric or nanometric particles [2, 11].

Manganese and cobalt oxides are useful, versatile and environmentally friendly catalysts which were extensively used for the oxidation of a variety of molecules, especially water oxidation, toluene oxidation, CO oxidation, carbon monoxide oxidation, the epoxidation of olefins and oxidative cyclization [12]. Herein, we developed a novel MOF route to prepare  $Mn_2O_3$ ,  $Mn_3O_4$ and  $Co_3O_4$  NPs, which involves the processes of converting metal oxide subunits in MOF into primary metal oxide NPs. The prepared metal oxide NPs were employed as heterogeneous catalysts in olefins epoxidation.

The precursors of Manganese and cobalt-terephthalate MOFs,  $[Mn_3(BDC)_3(DMF)_4]_n$  and  $[Co_3(BDC)_3(DMF)_2(H_2O)_2]_n$ , were prepared previously [13, 14] and used for the production of manganese and cobalt oxide NPs. The MOFs structures consist of M-O-C (M=Mn and Co) units wherein the terephthalate links were coordinated with the metal centers to form a 2D-polymeric chain. The organic linker in framework was removed at high temperature, through calcination and M-O<sub>6</sub> octahedral subunits convert to metal oxide NPs. The complete decomposition of MOFs occurred at the temperature above 320 °C for  $[Co_3(BDC)_3(DMF)_2(H_2O)_2]_n$  and 520 °C for  $[Mn_3(BDC)_3(DMF)_4]_n$  based on TG curves (Fig. 1S). So, calcination temperature for synthesized NPs was selected according to MOFs decomposition temperature. The Mn<sub>3</sub>O<sub>4</sub> NPs were obtained as a fine brown powder using  $[Mn_3(BDC)_3(DMF)_4]_n$  via a solid-state thermal decomposition route at 500 °C after 4h and Mn<sub>2</sub>O<sub>3</sub> NPs as black powder at 600 °C after 6h. The MOF of  $[Co_3(BDC)_3(DMF)_2(H_2O)_2]_n$  was used as a precursor to produce Co<sub>3</sub>O<sub>4</sub> NPs at 400 and 500 °C for 4 h in air at a heating rate of 3 °Cmin<sup>-1</sup>.

Comparing the FT-IR spectra of the two MOFs with samples after heating confirms that the templates have been completely destructed (Fig. 2S). Calcination of  $[Co_3(BDC)_3(DMF)_2(H_2O)_2]_n$  MOF at 400 or 500 °C indicates only two characteristic strong absorption bands at about 663.47 and 572.82 cm<sup>-1</sup> which are assigned to the Co-O stretching providing clear evidence for the presence of the crystalline spinel-type Co<sub>3</sub>O<sub>4</sub> structure [15]. After calcination of  $[Mn_3(BDC)_3(DMF)_4]_n$  MOF at 500 °C for 4h, three absorption peaks were observed at 400 to 650 cm<sup>-1</sup>. The vibration frequency at 639 cm<sup>-1</sup> is characteristic of Mn–O stretching modes in tetrahedral sites whereas vibration frequency at 533 cm<sup>-1</sup> corresponds to the distortion vibration of Mn–O in an octahedral environment. The third vibration band, located at a weaker wavenumber, 421 cm<sup>-1</sup>, can be attributed to the vibration of manganese species (Mn<sup>3+</sup>) in an octahedral site [16]. In calcinated [Mn<sub>3</sub>(BDC)<sub>3</sub>(DMF)<sub>4</sub>]<sub>n</sub> MOF at 600 °C for 6h, absorption peaks around 450-700 cm<sup>-1</sup> and the narrow one about 1650 cm<sup>-1</sup> correspond to the O-H vibrating mode of the adsorbed water in samples. The fingerprints of IR absorption at 400 to 700 cm<sup>-1</sup> for prepared samples confirmed metal-oxides formation by thermal decomposition MOFs templates.

The crystalline phase purity of the NPs was confirmed by powder XRD analysis. The XRD patterns of manganese oxide NPs indicated that calcinated sample at temperature of 500 °C has different crystallinity phase in comparison with calcinated sample at 600 °C (Fig. 1 (a) and (b)). The diffraction peaks of sample which was calcinated at 500 °C can be indexed to pure tetragonal phase of Hausmannite  $Mn_3O_4$  with the lattice parameters of a = 5.76, b = 5.76 and c = 9.44 Å, Z = 4 and S.G= I41/amd which are in JCPDS card file No. 24-0734 (Fig. 3S). The diffraction peaks of sample which was calcinated at 600 °C can be indexed to pure Cubic phase of Bixbyite  $Mn_2O_3$  with the lattice parameters of a = 9.41 Å, Z = 16 and S.G= Ia3 which are in JCPDS card file No. 10-0069 (Fig. 4S). The SEM images of prepared samples demonstrate that NPs have spherical shapes (Fig. 2). The average size of the particles calculated by the Scherer formula was 60 nm for  $Mn_3O_4$  (main (211) diffraction peak) and 80 nm for  $Mn_2O_3$  (main (222) diffraction peak) which are in agreement with TEM images (Fig. 3, c-f). As it is clearly noticeable in TEM images of  $Mn_2O_3$ , these NPs are agglomerated which can be achieved by the MOF route as Xu et al. revealed [18].

The XRD patterns of cobalt oxide NPs indicated that calcinated sample at 500 °C shows similar crystallinity with calcinated samples at 400 °C. The sharp peaks and higher signal to noise ratio indicate that the as-prepared Co<sub>3</sub>O<sub>4</sub> NPs are highly crystalline which can be further confirmed by the SEM images (Fig. 2). All the diffraction peaks of samples can be indexed to pure cubic spinel phase of Co<sub>3</sub>O<sub>4</sub> with the lattice parameters of a = 8.0837Å, Z = 8 and S.G= Fd3m with octahedrally coordinated Co<sup>3+</sup> and tetrahedrally coordinated Co<sup>2+</sup> which are in JCPDS card file No. 42-1467 (Fig. 5S). No impurity characteristic peaks related to CoO and Co<sub>2</sub>O<sub>3</sub> phases were detected. The SEM images of prepared samples show that Co<sub>3</sub>O<sub>4</sub> NPs have uniform fine spherical shapes. The particles size of the prepared sample were found to be about 40 nm which was calculated through the major (222) diffraction peak using the Debye Scherrer approximation which are in agreement with TEM images (Fig. 3, a, b).

The catalytic potential of NPs was examined in the olefins oxidation in the presence of *tert*buthylhydroperoxide (TBHP). In order to choose a suitable solvent, the oxidation of cyclooctene (as a model substrate) was carried out in dichloromethane, chloroform, acetonitrile, acetone, methanol and a mixture of  $CH_3OH/CH_2Cl_2$  (1:1). The results demonstrated that  $CH_3CN$  was a more efficient solvent and  $Mn_2O_3$  NPs are not as efficient as  $Co_3O_4$  and  $Mn_3O_4$  NPs (Table 1S). It seems that the oxidation state of Mn could play a key role in determining the catalytic behavior of the manganese oxide species. This can well account for the superiority of Mn(II) in comparison with other manganese oxidation states [19]. Aromatic and aliphatic alkenes react with TBHP to produce the corresponding epoxides and/or oxides (Table 1) in the presence of spinel type nanocatalysts. The catalytic oxidation reaction shows that nanocatalysts are superior for oxidation of cyclic (entry 1, 2) and aromatic olefins (entries 3-5) with good yield and moderate selectivity but are not efficient for oxidation of linear olefins (entry 6, 7).

The study on the catalytic activity of parent MOFs  $([Mn_3(BDC)_3(DMF)_4]_n$  and  $[Co_3(BDC)_3(DMF)_2(H_2O)_2]_n)$  and obtained  $Mn_3O_4$  and  $Co_3O_4$  NPs reveal that the extended structure and steric effects of MOFs make them weak catalysts compared to NPs. The results of olefin oxidations confirm that NPs are superior in conversion and catalytic reaction time [13, 14].

Since cyclohexene is a substrate that is particularly prone to allylic oxidation, its oxidation was studied in the presence of  $Co_3O_4$  and  $Mn_3O_4$  NPs to pursue the catalytic mechanism. The catalytic oxidation of cyclohexene, provided 2-cyclohexene-1-ol (80% for  $Co_3O_4$  and 88% for

 $Mn_3O_4$  NPs) in 95% and 90% conversion, respectively (Table 2, entry 2). Also, oxidation of styrene in the presence of  $Co_3O_4$  and  $Mn_3O_4$  nanocatalysts, involves C=C bond breaking, yielding styrene oxide (65 and 61%) with benzaldehyde (35 and 39%) (Table 1, entry 3). These oxidation products firmly imply a dominant radical pathway for this oxidation reaction, as was expected on the basis of other Mn(II) or Co(II) heterogeneous catalysts [13, 14, 19, 20]. To probe into the in situ formation of radical species in the oxidation reaction, ionol (2,6-di-tertbutyl-p-cresol) was utilized as a radical scavenger in the oxidation of styrene and cyclohexene. Oxidation was thoroughly inhibited in the presence of ionol which confirmed the formation of a radical intermediate in the reaction pathway. Probably, the Mn(II) and Co(II) catalyze homolytic O–O bond cleavage in t-BuOOH and alkoxy (t-BuO') radicals which are produced start the oxidation reaction. In the end, the olefin is oxidized to corresponding oxide/epoxide products.

The recyclability of the  $Mn_3O_4$  and  $Co_3O_4$  NPs catalysts was investigated in oxidation reaction of cyclooctene in the presence of TBHP in CH<sub>3</sub>CN at 75 °C for 7 h. After the first catalytic reaction, the solid catalyst was easily isolated by centrifuge and recovered by being washed with solvent and dried at 70 °C and used for the next run under the same reaction condition as the first run. The  $Co_3O_4$  NPs could well be recycled for nine cycles with no significant loss in activity and selectivity. During reusability studies, ninth run provided 88% conversion and 90% selectivity in favor of cyclooctene epoxide. The  $Mn_3O_4$  NPs could be recycled four cycles with no significant loss in activity and selectivity (Table 2). Therefore,  $Co_3O_4$  NPs are more efficient from reusability point of view.

The XRD patterns and IR spectroscopy showed that the catalysts have nearly identical peaks before and after catalytic reaction (Fig. 3, d, e and Fig. 2S, f, g), indicating that the basic lattice structures of these NPs were well maintained after catalysis. The amount of solved Co and Mn was found to be less than 1% by ICP analysis. This suggests that there is almost no Co and Mn in the liquid phase from these catalysts and the nature of catalytic reactions is heterogeneous.

 $Co_3O_4$ ,  $Mn_3O_4$  and  $Mn_2O_3$  NPs have been prepared by solid-state thermal decomposition from manganese and cobalt-terephthalate Metal Organic Frameworks by heating at 400, 500 and 600 °C. This synthetic route is a simple method for the preparation of uniform and high pure  $Co_3O_4$ ,  $Mn_3O_4$  and  $Mn_2O_3$  NPs with average size of 40, 60 and 80 nm respectively. The results of catalytic study exhibited that prepared NPs are active and selective heterogeneous catalysts for

olefins oxidation with the TBHP oxidizing agent in acetonitrile solvent.  $Co_3O_4$  and  $Mn_3O_4$  NPs can simultaneously provide high activity and selectivity to epoxide, easy separation of catalyst and appropriate performance in the recycling reaction. It was found that  $Co_3O_4$  presented superior performance to  $Mn_3O_4$  and  $Mn_2O_3$  in oxidation reaction in the case of reusability.

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**Fig. 1**. XRD pattern of prepared Mn<sub>3</sub>O<sub>4</sub> (a), Mn<sub>2</sub>O<sub>3</sub> (b), Co<sub>3</sub>O<sub>4</sub> (c) fresh nanoparticles and Mn<sub>3</sub>O<sub>4</sub> after fourth run (d) and Co<sub>3</sub>O<sub>4</sub> after ninth run (e) in catalytic cyclooctene oxidation.



Fig. 2. SEM images of  $Co_3O_4$  (a, b),  $Mn_3O_4$  (c, d) and  $Mn_2O_3$  (e-h) prepared nanoparticles.



Fig. 3.TEM images of  $Co_3O_4$  (a, b),  $Mn_3O_4$  (c, d) and  $Mn_2O_3$  (e, f) nanoparticles.

Entry	Substrate	Catalyst	Conversion <sup>b</sup>	Selectivity <sup>c</sup>
-		-	(%)	(%)
1	cyclooctene	$Co_3O_4$	98	95
		$Mn_3O_4$	95	95
		$[Mn_3(BDC)_3(DMF)_4]_n$	66 <sup>d</sup>	86
		$[Co_3(BDC)_3(DMF)_2(H_2O)_2]_n$	67 <sup>e</sup>	100
			$\sim$	C
2	cyclohexene	$Co_3O_4$	95	$15(80)^{r}$
		$Mn_3O_4$	90	$10(88)^{r}$
		C		
3	styrene	Co <sub>3</sub> O <sub>4</sub>	92	65
		$Mn_3O_4$	85	61
				100
4	trans-	Co <sub>3</sub> O <sub>4</sub>	80	100
	stylbene		77	100
		$Mn_3O_4$	/5	100
5	Indono	Call	65	100
3	mdene		03	100
		Mn <sub>3</sub> O <sub>4</sub>	60	100
6	1 hantana		17	100
0	1-neptene		17	100
		MII <sub>3</sub> O <sub>4</sub>	12	100
7	1_decene	CorO	15	100
1	1-decene	Mn <sub>2</sub> O	10	100
			10	100

**Table 1**. Oxidation of olefins catalyzed by metal-oxide nanoparticles<sup>a</sup>.

<sup>a</sup>Reaction condition: The reactions were run in CH<sub>3</sub>CN(2 mL) at 75 °C for 7 h by amount of 0.01 mmol catalyst, 1 mmol chlorobenzene, 1 mmol substrate and 1mmol TBHP. The molar ratio for catalyst: substrate: TBHP is 1: 100: 100.

<sup>b</sup>Conversion determined by GC based of chlorobenzene as internal standard. <sup>c</sup>Selectivity (%) to epoxide.

<sup>d</sup>Reaction in 1,2-dichloroethane for 9 h [13]. <sup>e</sup>Reaction in 1,2-dichloroethane for 7 h [14].

<sup>f</sup>Selectivity (%) to cyclohexene-1-ol as a main product.

Table 2. Reusability investigation of nanoparticles catalyst in oxidation of cyclooctene by TBHP<sup>a</sup>.

Entry	Catalyst (NPs)	Time (h)	Conversion <sup>b</sup> (%)	Selectivity <sup>c</sup> (%)
Run 1	$Mn_3O_4$	7	95	95
	$Co_3O_4$	7	98	95
Run 2	$Mn_3O_4$	7	100	93
	$Co_3O_4$	7	100	95
Run 3	$Mn_3O_4$	7	95	94
	$Co_3O_4$	7	100	95

Run 4	$Mn_3O_4$	7	85	92
	$Co_3O_4$	6	98	93
Run 5	$Co_3O_4$	6	92	94
Run 6	$Co_3O_4$	6	100	95
Run 7	$Co_3O_4$	7	99	94
Run 8	$Co_3O_4$	6	92	92
Run 9	$Co_3O_4$	6	88	90
ion condition	n: same as Table 1.7	The molar ratio	for catalyst: cycloo	octene: TBH
			0-	
			()	
			$\langle \mathcal{O} \rangle$	
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	()			
7				
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<sup>a</sup>Reaction condition: same as Table 1.The molar ratio for catalyst: cyclooctene: TBHP is 1: 100: 100.

#### **Graphical abstract: Synopsis**

#### Manganese and Cobalt-terephthalate Metal-Organic Frameworks as a Precursor for Synthesis of Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub> Nanoparticles: Active Catalysts for Olefin Heterogeneous Oxidation

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Spinel structured  $Mn_3O_4$  and  $Co_3O_4$  and  $Mn_2O_3$  nanoparticles were prepared by thermal decomposition of manganese and cobalt-terephthalate Metal-Organic Framework (MOF) precursor at 400, 500 and 600 °C. Scanning electron microscopy, transmission electron microscopy, Fourier transform infrared and X-ray diffraction spectrometry were used to characterize the phase and the morphology of the metal oxide nanoparticles. Characterization of prepared nanoparticles were indicate that these nanoparticles have average size diameter 60, 40 and 80 nm for  $Mn_3O_4$ ,  $Co_3O_4$  and  $Mn_2O_3$  respectively. Catalytic efficacy of  $Mn_3O_4$  and  $Co_3O_4$  nanoparticles were evaluated in the epoxidation of a variety of alkenes using *tert*-butyl hydroperoxide as an oxidant. In addition, metal oxide nanoparticles exhibited excellent catalytic stability in several runs, demonstrating that these heterogeneous and recyclable catalysts are promising for olefin epoxidation.





Highlights

►  $Co_3O_4$ ,  $Mn_3O_4$  and  $Mn_2O_3$  nanoparticles (NPs) were prepared by hydrothermal decomposition of  $[Co_3(BDC)_3(DMF)_2(H_2O)_2]_n$  and  $[Mn_3(BDC)_3(DMF)_4]_n$  MOFs.

► These NPs exhibit excellent catalytic activity and stability in olefins oxidation.

► High activity and selectivity to epoxide, easy separation and appropriate performance in the recycling reaction, make these NPs valuable.

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