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Core-shell Co-MOF-74@Mn-MOF-74 Catalysts with Controllable Shell Thickness and Their Enhanced Catalytic Activity for Toluene Oxidation

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Abstract: A series of core-shell Co-MOF-74@Mn-MOF-74 samples with different shell thicknesses were prepared by the seed growth method, which were characterized by powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), inductively coupled plasma mass spectrometry (ICP-MS), X-ray photoelectron spectroscopy, nitrogen adsorption-desorption and scanning electron microscopy (SEM). The shell thickness of these MOF samples were successfully controlled by adjusting the mass ratio between MnCl₂·4H₂O and Co-MOF-74. On this basis, these MOFs were applied to the catalytic oxidation of toluene. The results showed that with the growth of Mn-MOF-74 in the outer layer of Co-MOF-74, the oxidative selectivity of the substrate to benzaldehyde was greatly improved for the synergy between the core layer and shell layer. The conversion of toluene was 22.4%, and the selectivity of benzaldehyde was 98.1%. In addition, the catalyst can transform various substituted toluene into the corresponding aldehydes in highly selectivity and still keeps good stability after four catalytic cycles. The selectivity of the corresponding aldehyde is generally above 80 %.

Keywords: Metal-organic frameworks; Core-shell; Selective oxidation; Synergistic effect

1. Introduction

Aromatic alcohols, aromatic aldehydes and aromatic acids are a class of important intermediates used in pesticide and medicine, which are produced by oxidation of corresponding aromatic methyl derivatives.¹⁻³ In industry, aromatic methyl derivatives are often oxidized by KMnO₄, H₂SO₄, H₂O₂, bromide, etc., which could cause a lot of pollution and corrosion of equipments.^{2, 4} It is urgent to prepare new green and efficient catalysts to solve the defects of traditional catalysts, such as high pollution and strong corrosion. In the study of toluene oxidation, the researchers found that TBHP (tert-butyl hydroperoxide) could generate free radical substances in the condition of transition metal catalyst, which would lead to further oxidation of toluene.⁵ In this process, the metal ion can crack the weak O-O bond on TBHP to form *tert*-butyl peroxic radicals, which can react with the substrate in an oxygen atmosphere to produce corresponding oxides.^{6, 7} However, conventional metal catalysts are often homogeneous, which greatly limits the reuse of catalysts. Meanwhile, heterogeneous transition metal catalysts can be reused many times, while maintaining high catalytic oxidation activity.

Metal-organic Frameworks (MOFs) is a kind of porous crystal material composed of metal clusters connected by organic ligands.⁸ Due to its ordered pore structure, large specific surface area, easy surface modification and good thermochemical stability, the potential applications of MOFs in gas storage and separation,^{9, 10} heterogeneous catalysis,¹¹⁻¹⁴ ion detection¹⁵ and biomedicine^{16, 17} have attracted wide attention. Especially for the advantages of catalytic efficiency, easy

separation and reuse, MOFs have attracted wide attention in the field of heterogeneous catalysis^{11, 18-21} Among these MOFs, M-MOF-74 is a kind of MOF material with 2,5-dihydroxyterephthalic acid as organic ligand and different transition metals as nodes. Among them, the Co-MOF-74 material has high stability and abundant coordination unsaturated metal sites, which can be used as the active site of catalytic reaction to improve its catalytic activity.^{22, 23} In addition, the introduction of Mn²⁺ can enhance the adsorption capacity of the catalyst to toluene molecules and increase the alkaline sites on the catalyst surface, thus improving the selectivity of benzaldehyde.⁶ Furthermore, the hybrid structure of MOF was beneficial to the catalytic activity of catalysts.^{12, 24}

Core-shell MOF@MOF composites prepared by encapsulating one MOF within another can retain the chemical, physical, and structural advantages of both MOFs.²⁵ ^{26, 27} Moreover, MOF@MOF structures may produce some unexpected synergistic effects.²⁸ As is known, the core–shell catalyst can not only maintain the excellent performance of both core and shell materials, but also effectively overcome the disadvantages of single materials, exhibiting properties that are different from those of core or shell of MOFs.^{24, 25, 29, 30} Wang³¹ reported a novel UiO-67@Ni-MOF composite-based electrochemical sensor for nonenzymatic glucose sensing. The synergistic effect between good conductivity of UiO-67 and excellent electrocatalytic activity of Ni-MOF toward glucose made the composite a novel electrode material for glucose sensing. Zhang group²⁵ prepared ZIF-67@Co-MOF-74 catalyst by coating 2,5-dihydroxyterephthalic acid molecule on the surface of ZIF-67 crystal *via* the

ligand exchange method for light-driven water oxidation reaction. The core–shell MOFs show enhanced catalytic performance for the water oxidation reaction compared to individual ZIF-67 or Co-MOF-74 because of the synergistic effects between ZIF-67 and Co-MOF-74. Based on the significant advances of the core-shell MOFs, it is clear that the catalytic properties of the core-shell materials can be greatly improved by synergistic effects. Also, this feature will be beneficial to improve the catalytic activity in the oxidation of aromatic methyl derivatives.

In this study, a series of Co-MOF-74@Mn-MOF-74 samples were prepared. The shell thickness of Co-MOF-74@Mn-MOF-74 was successfully controlled by the mass ratio of Co-MOF-74 and MnCl₂·4H₂O. The growth of Mn-MOF-74 out of the Co-MOF-74 can expose more active sites to improve the catalytic activity. In addition, the interface of core-shell MOFs could be more conducive for rapid electron transport, which is helpful for the effective separation of electrons and holes to sufficiently inhibit charge recombination, resulting in effective increase in the interfacial charge transfer rate. Their structures and compositions were confirmed by powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), inductively coupled plasma mass spectrometry (ICP-MS), X-ray photoelectron spectroscopy, nitrogen adsorption-desorption and scanning electron microscopy (SEM). These materials were used as catalysts for catalytic oxidation of toluene, and the influences of catalyst structure on the oxidation reaction were studied. Among these core-shell MOF@MOF composites, Co-MOF-74@Mn-MOF-74-4 sample shows the best catalytic activity with 22.4 % toluene conversion and 98.1 % benzaldehyde selectivity. Besides, the

substrates were expanded and the catalysts showed good catalytic activity to all these substrates. In addition, the stability of these catalysts as well as the possible reaction mechanism were also investigated and discussed.

2. Experimental section

2.1 Materials

2,5-dihydroxyterephthalic acid (H₄DOBDC), cobalt nitrate hexahydrate $(Co(NO_3)_2 \cdot 6H_2O)$, polyvinylpyrrolidone (PVP) and tetrahydrate manganese chloride (MnCl₂·4H₂O) were purchased from Energy Chemical Co., Ltd. TBHP (50 %), *N*,*N*-dimethylformamide (DMF), acetonitrile (MeCN), ethanol (EtOH), deionized water (H₂O), toluene and methanol (MeOH) were obtained from Sinopharm Chemical Co., Ltd without further purification.

2.2 Synthesis of Co-MOF-74

Co-MOF-74 were synthesized by modifying the synthetic method reported in the previous literature.³² 2,5-Dihydroxyterephthalic acid (H₄DOBDC, 0.30 g, 1.51 mmol) and Co(NO₃)₂·6H₂O (0.73 g, 3.03 mmol) were added into a 60 mL mixture solution of EtOH, H₂O and DMF (1:1:1). Above mixture was stirred rapidly to obtain the homogeneous solution. The solution was transferred into 100 mL autoclave, and then heated at 150 °C for 24 h. After reaction, the solid was obtained by filtration and washed by DMF and MeOH for three times. After that, the as-synthesized materials were dried under vacuum at 150 °C for 12 h to obtain final Co-MOF-74.

2.3 Synthesis of Co-MOF-74@Mn-MOF-74

he catalyst by improving the seed growth method reported in the literature.²⁸ 0.10 g Co-MOF-74 seed, 0.50 g PVP and a certain amount of $MnCl_2 \cdot 4H_2O$ were added into 60 mL DMF, and then ultrasonic dispersion for 30 min. After that, H₄DOBDC (0.10 g, 0.51 mmol) was added into the above solution and then stirred for several minutes to obtain a homogeneous solution. The solution was transferred into 100 mL autoclave, and then heated at 150 °C for 24 h. After reaction, the solid was obtained by filtration and washed by DMF and MeOH for three times. After that, the as-synthesized materials were dried under vacuum at 150 °C for 24 h to obtain final Co-MOF-74@Mn-MOF-74-*x*. *x* represents the mass ratio between $MnCl_2 \cdot 4H_2O$ and Co-MOF-74.

2.4 Catalyst characterization

PXRD analyses were carried out on a Rigaku MiniFlex 600 with Cu Kα radiation from 3 to 50°. The specific surface area and distribution of pore size were determined on a Micromeritics ASAP 2460 apparatus using the Brunauer-Emmett-Teller (BET) method from N₂ adsorption-desorption. Before BET measurements, all samples were pretreated at 160 °C for 6 h under vacuum. The element content of cobalt was measured on an Agilent 7700 ICP-MS. SEM images were obtained on a Hitachi S-3400N II equipped with Energy dispersive X-ray (EX-250, Horiba) analysis operating at 30 kV.

2.5 Catalytic oxidation of toluene

The catalytic oxidation test of toluene was carried out under atmospheric pressure using oxygen as an oxidant. The following steps were taken: 15 mL Schlenk

tube was mixed with 30 mg as-prepared catalyst and additive 10 mol% TBHP, 28 mmol toluene and 3 mL MeCN, stirred at a certain temperature, and assembled with oxygen balloon (0.1 MPa). Meanwhile, the conversion of toluene and the selectivity of products were quantitatively analyzed by high performance liquid chromatography (HPLC, P680A LPG-4).

3. Results and discussion

3.1 Catalyst structure characterization

The crystal structure of as-prepared MOFs was identified by PXRD. The PXRD pattern was shown in Figure 1 a. All the samples showed sharp and clear diffraction peaks, indicating that the highly crystallized samples were successfully synthesized. The peak at 2 θ = 6.7° in the XRD pattern of the sample belongs to the (110) crystal plane of the Co-MOF-74, while the peak at 2 θ = 11.7° belongs to the (300) crystal plane, which is consistent with the characteristic diffraction peaks reported in the literature.^{18, 33} Diffraction peaks of Co-MOF-74 and Co-MOF-74@MOF-74-x were quite similar and there were no redundant diffraction peaks, indicating that Co-MOF-74 is not destroyed in the synthesis process. There were no new diffraction peaks for Co-MOF-74@Mn-MOF-74-x, indicating that the material is a single phase crystal and no hybrid peaks were generated. Figure 1 b showed that after a layer of Mn-MOF-74 grew on the outer layer of Co-MOF-74, the diffraction peak originally located at 2 θ = 6.7° was shifted to the left due to the lattice of Mn-MOF-74 is larger than that of Co-MOF-74. The lattice enlargement is mainly due to the difference of radius of Mn (97.0 pm) and Co (88.5 pm). The Mn-MOF-74 growing in the outer

layer made the original lattice larger, so that the diffraction peak was shifted to a small angle. ³⁴⁻³⁶ Moreover, as the thickness of Mn-MOF-74 increased, this trend became more obvious. This indicated that the Co-MOF-74@Mn-MOF-74-x (x = 1, 2, 4) had been successfully synthesized.



Figure 1 Powder XRD patterns of different, (a) 2 Theta = $5 - 40^{\circ}$, (b) 2 Theta = $5 - 8^{\circ}$

Samples	The content of Co (wt.%)	The content of Mn (wt.%)
Co-MOF-74	27.66	-
Mn-MOF-74	-	24.44
Co-MOF-74@Mn-MOF-74-1	21.17	6.11
Co-MOF-74@Mn-MOF-74-2	16.87	10.72
Co-MOF-74@Mn-MOF-74-4	10.96	17.72

Table 1 Co and Mn element composition of different samples

The morphology and size of all the MOFs were characterized by SEM. Figure 2 showed the SEM images of Co-MOF-74. The results showed that Co-MOF-74 has uniform rod-like six-prism structure and smooth surface. The length of the rod was between 70 and 100 μ m. The Co-MOF-74@Mn-MOF-74-*x* obtained by epitaxial growth exhibit the same morphology, which indicated that the structure of Co-MOF-74 was not damaged during epitaxial growth. This conclusion is also confirmed by the PXRD. In addition, Figure 3 illustrated the EDS mapping of Co-MOF-74@Mn-MOF-74-*x* with different thicknesses. The results showed that the shell thickness of Mn-MOF-74 increased with the increase of MnCl₂·4H₂O mass, indicating that Co-MOF-74@Mn-MOF-74-*x* were successfully synthesized and their shell thickness could be regulated by changing the mass ratio between MnCl₂·4H₂O and Co-MOF-74.

As is shown in Figure 3 (a-d), when the mass ratio was 1:1, there is a thin layer of Mn-MOF-74 wrapped around the outer layer of Co-MOF-74. The thickness of Mn-MOF-74 was less than 1 μ m. When the mass ratio increased to 2:1, the thickness

of the Mn-MOF-74 layer gradually increased, as shown in Figure 3 (e-h). Furthermore, when the mass ratio was 4:1, it can be seen from Figure 3 (i-l) that the thickness of Mn-MOF-74 increased to about $2 \mu m$.

The contents of Co and Mn in the catalysts were measured by ICP-MS (Table 1). The element compositions of Co and Mn element composition were 27.66 % and 24.44 % for Co-MOF-74 and Mn-MOF-74, respectively. Similarly, with the increase of introduced Mn ion, the content of Mn increased from 6.11 % to 17.72 %, while the content of Co decreased from 21.17 % to 10.96 %, which reflected the increase of shell thickness.



Figure 2 SEM of different Co-MOF-74



Figure 3 SEM and mapping images of different Co-MOF-74@Mn-MOF-74: (a-d)

Co-MOF-74@Mn-MOF-74-1; (e-h) Co-MOF-74@Mn-MOF-74-2; (i-l)

Co-MOF-74@Mn-MOF-74-4

The surface element composition and chemical states of the all samples were measured by XPS, as displayed in Figure 4. The XPS spectra of Co-MOF-74, Mn-MOF-74, and Co-MOF-74@Mn-MOF-74-4 were illustrated in Figure 4 (a), where C 1s (284.08 eV) and O 1s (531.08 eV) were all found in three samples. After epitaxial 641.8 observed growth, peak eV in а new at was Co-MOF-74@Mn-MOF-74-4, which was attributed to the introduction of Mn-MOF-74. The Co 2p signal from Co-MOF-74 and the Mn 2p signal from Mn-MOF-74 were observed to coexist in Co-MOF-74@Mn-MOF-74-4, thereby indicating the successful combination of Co-MOF-74 and Mn-MOF-74.





Figure 4 (a) XPS spectra of prepared Co-MOF-74, Mn-MOF-74, Co-MOF-74@Mn-MOF-74-4; (b)

Mn 2p signal deconvolution; (c) Co 2p signal deconvolution

In In order to evaluate the thermal stability of the catalysts, TGA was used under flowing air, and the curve was shown in Figure 5. All the samples showed two kinds of weightlessness in the range of room temperature to 500 °C. The weight loss in range of 100-150 °C should mainly be caused by the evaporation of water and DMF in the channel. The second weight loss in the range of 250-330 °C could be attributed to the decomposition of the organic linkers and the corresponding metallic oxide (such as Mn_3O_4 and Co_3O_4) remained as a residue. These results indicated that the catalysts were still stable at about 300 °C, which can avoid deactivation of catalysts due to decomposition in the reaction process.



Figure 5 TG curves of different samples

The porosity and specific surface of Co-MOF-74 and area Co-MOF-74@Mn-MOF-74-x catalysts were tested by nitrogen adsorption. The N_2 adsorption/desorption isotherms of the catalysts were characterized at 77 K, and the isotherms of the types of MOFs were type IV according to the IUPAC classification of isotherm shapes (Figure 6 a).³⁷ It can be found that the specific surface area of Co-MOF-74 and Mn-MOF-74 were 427 m²/g and 1031 m²/g, respectively, and the specific surface area of Co-MOF-74@Mn-MOF-74-x ranged from 597 to 941 m²/g. With the increase of shell thickness, the specific surface area of core-shell MOF increases gradually. The average adsorption pore diameter of Co-MOF-74 and Mn-MOF-74 were 2.69 nm and 3.5 nm, respectively, while the pore diameter of Co-MOF-74@Mn-MOF-74-x ranged from 2.98 to 4.49 nm. The increase in pore size is mainly attributed to the growth of outer Mn-MOF-74. The increased pore size can provide more reactive sites to improve the catalytic activity.



Figure 6 a) Nitrogen adsorption-desorption isotherms, and b) pore size distributions of

Co-MOF-74, Mn-MOF-74 and Co-MOF-74@Mn-MOF-74-x

3.2 Catalytic activity of catalysts in oxidation of toluene.

On the basis of synthesizing Co-MOF-74@Mn-MOF-74-x with different shell thicknesses, their catalytic activity in toluene oxidation were evaluated by using

oxygen as oxidant and TBHP as promoter at 80 °C for 6 h . As shown in Table 2, the catalyst exhibited good catalytic activity for toluene, and the main products were corresponding alcohols, aldehydes and acids.

For the blank experiment without catalyst, it can be seen that the conversion of toluene is very low and the reaction can hardly occur, suggesting that the catalyst plays a key role in the oxidation of toluene. Simultaneously, the control experiment showed that TBHP was not added in the reaction, the conversion of toluene dropped sharply to 3.2 % (Table 2, Entry 9), which indicated that TBHP was a key promoter in the reaction. When Co(NO₃)₂ was used as catalyst, the conversion rate of toluene reached 18.3 %, but after researching the selectivity of the product, it was found that the product was mainly converted to benzoic acid, reaching 57.1 % (Table 2, Entry 2). Although Co(NO₃)₂ has high catalytic conversion and benzoic acid selectivity, it cannot be reused after the reaction, also resulting in pollution and waste.

When Co-MOF-74 was used as catalyst, the conversion of toluene reached 16.7 %. The main product of oxidation was benzaldehyde, and the selectivity of benzaldehyde reached up to 60.0 %, which was quite different from that of $Co(NO_3)_2$. This is mainly because the Co content in Co-MOF-74 is much lower than that in $Co(NO_3)_2$, thus benzaldehyde cannot be further oxidized to benzoic acid.³⁸ Compared with Co-MOF-74 catalyst, the Mn-MOF-74 catalyst showed higher selectivity of benzaldehyde, reaching 80.3 %. However, the conversion of toluene for Mn-MOF-74 was lower than that of Co-MOF-74, reaching just 13.2 % (Table 2, Entry 4). These results indicated that Co-MOF-74 facilitated the catalytic transformation of toluene

oxidation and Mn-MOF-74 benefited the formation of benzaldehyde. Based on the above results, we used Co-MOF-74 as the main constituent of the catalyst and introduced the Mn-MOF-74 with the aim of achieving a high catalytic activity and a high selectivity of benzaldehyde *via* the synergy between shell layer and core layer.

The catalytic activities of Co-MOF-74@Mn-MOF-74-*x* catalysts were explored and the results were listed in Table 2. It was found that all the Co-MOF-74@Mn-MOF-74-*x* catalysts obtain a good conversion of toluene while maintaining a high selectivity of benzaldehyde. The conversion of toluene ranged from 18.5 % to 22.4 % and the selectivity of benzaldehyde changed from 92.6 % to 98.1 % with the shell growth (Table 2, Entry 5-7), which were higher than single Co-MOF-74 and Mn-MOF-74.

There are four main reasons for the increasing conversion of toluene. First of all, introduced Mn-MOF-74 as a shell layer can enhance the interaction between toluene and catalyst in the catalytic system, allowing more substrates to participate in the reaction.⁶ Furthermore, with the growth of Mn-MOF-74 in outer of the Co-MOF-74, the number of active sites (Mn sites) and the specific surface area are increased and then enhance the conversion of substrates. Additionally, the surface of core-shell catalyst is no longer smooth, which exposes more active sites of the metal and allows the catalyst to come into full contact with the substrate molecule.²⁵ Finally, the interface of core-shell MOFs is more conducive for rapid electron transport, which is helpful for the effective separation of electrons and holes to sufficiently inhibit charge recombination,³⁹ resulting in effective increase in the interfacial charge transfer rate.

When the Co-MOF-74@Mn-MOF-74-*x* was used as catalyst, the selectivity of benzaldehyde ranged from 92.6 % to 98.1 %, which was better than single Co-MOF-74 or Mn-MOF-74. The increased selectivity was mainly due to the synergistic effect between Co-MOF-74 and Mn-MOF-74 in the process of reaction. More specifically, when the substrate molecules and TBHP contacted with the nuclear layer of Co-MOF-74 through the catalyst channel, the Co metal site of Co-MOF-74 can generate peroxy radical by cracking TBHP *via* Haber-Weiss route. Subsequently, when the main oxidation products benzyl alcohol and benzaldehyde were desorbed from the pore channels of the Co-MOF-74, the Mn metal site in Mn-MOF-74 could rapidly further oxidize benzyl alcohol to benzaldehyde for the presence of base side of Mn-MOF-74 and desorbed from the Mn-MOF-74 pore channels with the original benzaldehyde. This explained that the Co-MOF-74@Mn-MOF-74-*x* catalysts exhibit excellent selectivity of benzaldehyde, while still having a good conversion of toluene.

Among the Co-MOF-74@Mn-MOF-74-*x* catalysts, the Co-MOF-74@Mn-MOF-74-4 catalyst showed the best catalytic activity compared with Co-MOF-74@Mn-MOF-74-1 and Co-MOF-74@Mn-MOF-74-2, which obtained a toluene conversion of 22.4 % and a benzaldehyde selectivity of 98.1 % (Table 2, Entry 7). As we all know, the composition of catalysts will influence the activity of catalytic reactions when the reaction conditions remain unchanged. In this system, the difference of catalyst mainly lies in the thickness of Mn-MOF-74. In short, the catalytic activity of a catalyst is affected by the thickness of shell. The presence of Mn ions can enhance the adsorption capacity of the catalyst to toluene molecules, which

has been mentioned above. And with the increase of Mn content, the catalyst can absorb more substrate molecules. ICP-MS showed the content of Mn element increased with the growth of shell thickness. When the mass ratio between MnCl₂·4H₂O and Co-MOF-74 is 4:1, the content of Mn element in the Co-MOF-74@Mn-MOF-74-4 is 17.72 % which is higher than that of Co-MOF-74@Mn-MOF-74-1 (6.11 %) and Co-MOF-74@Mn-MOF-74-2 (10.72 %). Furthermore, the specific surface area of Co-MOF-74@Mn-MOF-74-4 is 941 m²/g, which is higher than that of other core-shell catalysts from Figure 6. It is well known that the greater the specific surface area of the catalyst, the more active sites it can provide to enhance the catalytic activity. These explain the superior catalytic activity of Co-MOF-74@Mn-MOF-74-4 compared with other core-shell catalysts.

C	CH ₃ Catalyst, TBHP, O ₂	CH₂OH	сно	çc	ЮН	
	CH ₃ CN			+		
Entry	Catalyst	Conversion/% —	S	Selectivity ^b /%		
			BAL	BA	BAC	
1	-	1.9	30.1	60.3	-	
2	$Co(NO_3)_2$	18.3	22.3	12.1	57.1	
3	Co-MOF-74	16.7	38.1	60.0	1.8	
4	Mn-MOF-74	13.2	8.7	80.3	-	
5	Co-MOF-74@Mn-MOF-74-1	18.5	5.4	92.6	1.4	
6	Co-MOF-74@Mn-MOF-74-2	20.2	1.6	94.9	1.2	
7	Co-MOF-74@Mn-MOF-74-4	22.4	0.7	98.1	0.9	
8	Co-MOF-74+Mn-MOF-74	19.3	12.1	78.3	7.4	
9 ^c	Co-MOF-74@Mn-MOF-74-4	3.2	-	51.0	33.7	
10^{d}	Co-MOF-74@Mn-MOF-74-4	-	-	-	-	

Table 2 Oxidation of toluene catalyzed over different catalysts^a

^aReaction condition: 30 mg of catalyst, 3 mL toluene (28 mmol), O₂ balloon, 10 mol% TBHP, 3 mL CH₃CN, 80

^oC, 6 h, ^bBAC = selectivity of benzoic acid, BA = selectivity of benzaldehyde, BAL = selectivity of benzyl

alcohol, ^cWithout TBHP, 3 mL CH₃CN, 80 ^oC, 6 h, ^d1 eq. BHT.

To prove the synergistic effect between Co-MOF-74 and Mn-MOF-74, mixture of Co-MOF-74 and Mn-MOF-74 used as catalyst to oxidize toluene. The results were shown in Table 2, Entry 8. The catalytic activity of mixed catalyst (Co-MOF-74+Mn-MOF-74) quite different of was from that Co-MOF-74@Mn-MOF-74-4. The conversion of toluene catalyzed over mixed catalyst was 19.3 % and the selectivity of benzaldehyde was 78.3 %, which indicated that the separate Mn-MOF-74 cannot improve the catalytic activity of Co-MOF-74 compared with the Co-MOF-74@Mn-MOF-74-4. In other words, mixed catalyst composed of Co-MOF-74 and Mn-MOF-74 via physical mixing cannot play a synergistic role in the catalytic system to improve catalytic activity.

In order to expand the application of this catalyst, a series of toluene derivatives containing different substituents were selected and the result of oxidation to the corresponding aldehydes were summarized in Table 3. For the derivatives containing donor groups, the catalyst demonstrated excellent selectivity of aldehydes, but the relatively low conversion rate. For example, the conversion rate of *p*-xylene was 15.7 %, while the selectivity of the corresponding aldehyde reached up to 98.2 %. However, for some derivatives containing electron-absorbing groups, the catalyst also showed relatively low selectivity of corresponding aldehyde and high conversion rate. For example, the conversion rate. For example, the selectivity of corresponding aldehyde and high conversion rate. For example, the conversion of *p*-nitrotoluene and the selectivity of corresponding aldehyde was 22.1 % and 87.2 %, respectively. This is mainly due to the influence of different groups connected to toluene and different electron-supplying and adsorbing groups, which changes the C-H bond length on the methyl group. In addition, the

adsorption of substrates with different substituents in the catalyst channel is also different.

Ar-CHa	Co-MOF-74@Mn-MOF-74-4, TBHP, O ₂		Ar-CHO	Conversion [%],	
ni eng	CH ₃ CN, 80 ℃,	6 h, 0.1 Mpa		(Selectivity [%])	
			OCH ₃	t-Bu	NH ₂
15.7 (93	3.2) 13.8 (93.6)	19.1 (91.5)	11.3 (88.7)	10.9 (90.7)	9.3 (90.6)
Br		CI	NO ₂	CN	NO ₂
16.7 (84	4.9) 18.5 (94.1)	19.3 (95.2)	23.3 (83.2)	20.1 (81.2)	22.1 (87.2)

Table 3 Aerobic oxidation of various substituted toluenes over Co-MOF-74@Mn-MOF-74-4^a

^aReaction condition: 30 mg of catalyst, 3 mL toluene (28 mmol), O₂ balloon, 10 mol% TBHP, 3 mL CH₃CN, 80 ^oC, 6 h

Based on the existing experimental results and the reaction process reported by predecessors^{40, 41}, the experimental mechanism of catalytic oxidation of toluene by Co-MOF-74@Mn-MOF-74 under the conditions of oxygen and TBHP was supposed. Without TBHP in the catalytic system, the conversion of toluene was just 3.2 % (Table 2, Entry 9). Then, when the free radical scavenger 2, 6-2-*tert*-butyl, 4-methyl phenol (BHT) and TBHP were introduced together in the catalytic system (Table 2, Entry 10), the reaction did not occur. These results indicate that the reaction occurred

via a radical pathway. Therefore, there may be a free radical reaction course in this reaction.

Based on the above experiments, a possible reaction mechanism was proposed and shown in Figure 7. Toluene molecules and TBHP were absorbed by the catalyst and entered into the catalyst through the pore, and the Co site decomposed TBHP to produce *t*-BuOO•. *t*-BuOO• formed benzyl radicals by taking a hydrogen atom from the methyl group. This benzyl radical captured an activated oxygen molecule to form benzylperoxy radical. After that, the benzylperoxy radical reacted with TBHP/toluene to produce benzyl hydroperoxide. Benzyl hydroperoxide was rapidly oxidized by the Co metal site to form the intermediate benzyl alcohol. Benzyl alcohol was then desorbed from Co-MOF-74 to the shell, and Mn-MOF-74 can rapidly oxidize benzyl alcohol to benzaldehyde due to its own base site.



Figure 7 Proposed mechanism for the catalytic reaction of toluene over

Co-MOF-74@Mn-MOF-74

The stability of the catalyst before and after 4 cycles was determined by PXRD as shown in Figure 8. The diffraction peaks of used catalyst were the same as that of

fresh catalyst, and no new peaks were generated, which indicated that the overall structure of the catalyst did not change after the 4 cycles. Figure 9 displays the conversion of toluene and selectivity of benzaldehyde for subsequent oxidation experiments. The catalyst shows good reusability, and after four runs, the conversion rate of toluene is 15.4% and the selectivity of benzaldehyde is 89.9%. The results showed that the catalyst has good stability and can be used for the oxidation reaction.



Figure 8 PXRD patterns of the fresh and used for four times Co-MOF-74@Mn-MOF-74-4



catalyst in toluene oxidation

Figure 9 Catalyst reusability study of Co-MOF-74@Mn-MOF-74-4 in toluene oxidation

Conclusions

Co-MOF-74@Mn-MOF-74-*x* catalysts with core-shell structure were synthesized by epitaxial growth method, and their structure and composition were determined by different characterization techniques. The shell thickness of Co-MOF-74@Mn-MOF-74 was successfully controlled by adjusting the mass ratio between MnCl₂·4H₂O and Co-MOF-74. The Co-MOF-74@Mn-MOF-74-x catalysts were used in the oxidation of toluene, exhibited high selectivity of benzaldehyde and favorable conversion of toluene compared to single Co-MOF-74 or Mn-MOF-74. Among them, the Co-MOF-74@Mn-MOF-74-4 showed enhanced catalytic activity (22.4 %) and high selectivity towards benzaldehyde (98.1 %). The interaction between toluene and catalyst was also investigated, and the results indicate that the synergistic effect between Co-MOF-74 and Mn-MOF-74 could promote the conversion of toluene to benzaldehyde significantly. Furthermore, the catalyst can not only convert the toluene derivative to corresponding aldehyde, but also maintain high selectivity in the oxidation process. In addition, the catalyst can be reused for 4 times and has great potential in oxidation of toluene. These results indicate that compared to single MOF in oxidation toluene, the core-shell MOFs could achieve higher catalytic activity via synergistic effect between core and shell, which could be potentially used in the oxidation of aromatic methyl derivatives.

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Highlights

Co-MOF-74@Mn-MOF-74 catalysts were synthesized by seed growth method.

Shell thickness of Co-MOF-74@Mn-MOF-74 could be controlled.

The catalytic activity was enhanced via synergistic effect between core and shell.

These materials exhibit excellent catalytic activity in toluene oxidation.

Journal Pre-proof

Graphical Abstract

A series of core-shell Co-MOF-74@Mn-MOF-74 samples with different shell thickness were prepared by seed growth method. Their catalytic activity was enhanced *via* synergistic effect between core and shell in toluene oxidation. Furthermore, the shell thickness has influence on catalytic activity. The Co-MOF-74@Mn-MOF-74-4 sample exhibits the best catalytic activity with 22.4 % toluene conversion and 98.1 % benzaldehyde selectivity.

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

