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Size-selective catalysts in five functionalized porous coordination polymers with unsaturated zinc centers

Dongsheng Deng^a, Hui Guo^a, Baoming Ji^{a*}, Weizhou Wang^a, Lufang Ma^a and Feng Luo^{b*}

^a Henan Key Laboratory of Function-Oriented Porous Materials, and College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471934, P. R. China College of Biology, ^b Chemistry and Material Science, East China Institute of Technology, Fuzhou, Jiangxi, P. R. China.

(* Corresponding author Tel.: +86 379 65523821; fax: +86 379 65523821.

E-mail address: dengdongsheng168@sina.com; lyhxxjbm@126.com)

Abstract: The five reported structural isomorphic porous coordination polymers (PCPs) **1**–**5**, namely, [Zn(L)(ip) (1), Zn(L)(aip) (**2**), Zn(L)(hip) (**3**), Zn(L)(nip) (**4**), and Zn(L)(HBTC) (**5**) (L = N^4, N^4 '-di(pyridine-4-yl)biphenyl-4,4'-dicarboxamide, H₂ip = isophthalic acid, H₂aip = 5-aminoisophthalic acid, H₂hip = 5-hydroxyisophthalic acid, H₂nip = 5-nitroisophthalic acid, H₃BTC = 1,3,5-benzenetricarboxylic acid)] were used to catalyze acetylation of phenol. All these heterogeneous catalysts exhibit good catalytic efficiency and size-selectivity toward acetylation of phenols owing to their unsaturated metal centers, non-coordinated amide, and suitable channel size and shape. Among them, the **2** displays highest catalytic activity and excellent cooperative catalysis due to the present of basic non-coordinated amide groups.

1. Introduction

Catalysts based on rigid porous or channel frameworks possess the merits of both homogeneous and heterogeneous catalysts, and surmount all the limitations of the homogeneous catalysts, such as difficulty in separation and recovery and disposal of spent catalysts.¹⁻⁴ Considered to be promising analogues of inorganic zeolites, porous coordination polymers (PCPs) constructed by inorganic ions and organic linkers are nowadays at the front of materials research because of their intriguing structural architecture and outstanding functional properties.⁵⁻⁸

Generally, porous coordination polymers as heterogeneous catalysts should own the following features:^{9,10} 1) the three distinct components of PCPs, namely metal nodes, organic ligands and pores can all be easily tailored for their catalytic activities due to the modular nature and facile tenability of PCPs, combining the merits of inorganic and organic chemistry; 2) the open accessible channels or pores are beneficial for trapping substrates or activating of reactants, and the well-defined crystalline structure of PCPs is useful for elucidating structure-function relationships; 3) the existence of coordinatively unsaturated metal sites (UMS) or the introduction of functional organic sites (FOS) can

be used to decorate channel surfaces of PCPs; 4) as a solid materials, PCPs catalysts must be easy to separate from reaction system and can be reused for the next run, and thus reducing waste and contamination.

The exploiting of PCPs as heterogeneous catalysts has been accompanied by the massive growth of PCPs structural and functional complexity.¹¹⁻¹⁴ Among these studies, it is noted that UMS or FOS is indispensable in the catalytic system for the C–C bond formation reaction, where UMS or FOS can activate reaction substrates so as to promote the reaction smoothly. Meanwhile, a lot of reports have revealed that the unique merits of PCPs based UMS or FOS catalysis exceeds purely organic or inorganic systems.¹⁵⁻¹⁷ For example, Kitagawa and co-workers have designed and synthesized a 3D PCPs functionalized with amide groups.⁹ They showed that these amide groups locating on the channel surface can interact with guest molecules and selectively promote the Knoevenagel condensation reaction based on the relationship between the size of the reactants and the pore window of host. Next, Long and other group revealed that a 3D Mn PCPs was used as Lewis acid-type catalyst to catalyze cyanosilylation reaction with good substrate-size-selectivity.¹⁸ Lately, Duan and co-workers have isolated bi-functionalized PCPs for sequential multistep catalysis.¹⁹

Inspired by the above reaction principle, as an extension to our previous investigation,^{20,21} we pursue to evaluate the catalytic performance of the five Zn(II) PCPs with both UMS and different FOS in the framework, which are anticipated to be endowed with satisfactory activity for acetylation of phenols. As is well known, the acetylation of phenols is an important nucleophilic reaction for the synthetic organic chemist, which is often carried out under homogeneous conditions with acetic acid or acetyl chloride or anhydride, in the presence of basic catalysts such as pyridine or triethylamine.^{22,23} One drawback of this method is that base-sensitive substrates may result in decomposition. To address this issue, some PCPs have been found to be an ideal catalyst for the acetylation of phenols.^{24,25} For example, Moorthy *et. al.* demonstrated that the use of some PCPs based on a twisted tetrapyridylbiaryl ligand as catalysts, acetylation reactions of various phenols proceeded smoothly, and affording the corresponding products with excellent yields.²⁶ Thus, the development of suitable PCPs for this reaction is a top of great interest.

Herein, the present work aims at investigating the catalytic efficiency of different types of functional groups exposed in the pores toward the acetyl reactions, so as to find which material can exhibit cooperative effect on catalytic capacity or not. As a cooperative catalyst, 2 displays excellent catalytic ability for the acetylation of phenols. Based on the above-mentioned fact, we think that the presence of basic amine groups, the full accessible porosity, together with a high thermal and chemical stability can make 2 an excellent nucleophilic catalyst for acetylation of phenols.

2. Experimental Section

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2.1. General procedures

All chemicals were of reagent grade quality obtained form commercial sources and used as received unless special notice. Thermogravimetric analyses (TGA) were carried out on a SDTQ600 differential thermal analyzer with a heating rate of 10 °C/min in a N₂ atmosphere. Powder X-ray diffraction (PXRD) data were recorded with a Bruker D8-ADVANCE X-ray diffractometer by using $Cu_{K\alpha}$ radiation. ¹H NMR spectra were measured on a Varian UNITY/NOVA 400 NMR spectrometer using CDCl₃ as the solvent at room temperature. Chemical shifts are given in δ relative to TMS. The coupling constants *J* are given Hz.

2.2. The syntheses of 1–5

The polymers of **1–5** were prepared according to the literature method.²¹ A mixture of $Zn(NO_3)_2$ (38 mg, 0.2 mmol), L (79 mg, 0.2 mmol), multi-carboxylate ligand (H₂ip (33 mg, 0.2 mmol), or H₂aip (36 mg, 0.2 mmol), or H₂hip (36 mg, 0.2 mmol), or H₂nip(42 mg, 0.2 mmol), or H₃BTC(42 mg, 0.2 mmol) and DMF/H₂O (10 mL, 5:1) was sealed in a 23 mL Teflon-lined stainless steel container and heated at 120 °C for 2 days, and then cooled to room temperature at a rate of 3°C/h. The collected crystals were treated under vacuum at 100 °C for 12 h to obtain the full evacuated framework. The yields for **1–5** were 88%, 84%, 87%, 88% and 86% based on Zn, respectively.

2.3. Typical procedure for acetylation of phenols using 2 as catalyst

A capped vial was charged with acetic anhydride (1.5 mmol), phenol (0.5 mmol), catalyst (0.01 mmol) and CH_2Cl_2 (1 mL). The reaction mixture was stirred for the required time, and was monitored by TLC analysis. After completion of the reaction, 10 mL of ethyl acetate was added to the reaction mixture. The mixture was stirred for another 5 min. Then the catalyst was isolated by filtration and washed thoroughly ethyl acetate, and the filtrate was thoroughly washed with aqueous Na₂CO₃ solution to remove the unreacted anhydride and acetic acid. The organic layer was dried over anhydrous Mg₂SO₄ and evaporated to obtain the corresponding pure products. All isolated pure products were fully characterized by NMR analysis. The recovered catalyst was washed with ethyl acetate, dried, and reused without further purification or regeneration.

2.4. Experimental procedure for reusability tests

The reusability of **2** was tested for acetylation of phenols. When the reaction finished, the catalyst was isolated by filtration and washed thoroughly ethyl acetate, and the resulting catalyst was dried at 80°C for 4 h under vacuum, then reused directly without further purification for the second run with fresh acetic anhydride and phenol. It was used for four consecutive runs with minor loss in activity. Moreover, the recovered catalysts were characterized by the X-ray powder diffraction and showed identical results to those of the fresh samples.

3. Results and Discussion

The previous crystal structural analyses revealed that the compounds 1-5 are structural isomorphs.²¹ In the structures of 1-5, the unique Zn^{2+} ion is tetra-coordinated by two L ligand N atoms and two carboxylate O atoms in a distorted tetrahedral geometry, as observed in compound 2 (Fig. 1a). Moreover, the 1D regular hexagonal channels along the c axis are observed in their frameworks (Fig. 1b), which not only possess abundant amide groups but also is decorated by different functional groups of -H, -OH, -NH₂, -NO₂, and -COOH, respectively. The pore diameters are estimated in the range of 7.0-9.4 Å. Therefore, the five zinc PCPs have both coordinatively unsaturated Lewis acid (Zn^{2+}) centers, basic centers (amide groups), as well as other different organic functional groups (Fig. 1). These features imply that the presence of coordinatively unsaturated Zn(II) atoms allows their use as a Lewis acid, and the different FOS located around the cavity of the PCPs would provide a significant catalyzing force for special reactions. Because the zinc polymers (1-5)have different FOS, it would be interesting to see how the different functional features affect the catalytic behavior. As is well known, the thermal stability of catalysts is an important factor in evaluating their catalytic capacity. Therefore, it is necessary to investigate the thermal stability of 1-5. In this regard, thermogravimetric analysis experiments were performed for 1-5 under a N_2 atmosphere. As shown in Figure S1, the thermograms of 1-5 show similar profiles. The five compounds are thermally very stable up to 270 °C. Because there are no solvent molecules in the frameworks, there is a plateau region ranging from 25 to 330 °C in 1, 380 °C in 2, 375 °C in 3, 365 °C in 4, and 370 °C in 5, followed by a sudden decrease in the weight, suggesting the onset of the decomposition temperature of the compounds (see ESI[†] for details). The result reveals that these five compounds possess excellent structural stability.

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(b)

Fig. 1. Catalyst 2 structure: a) Coordination environment of Zn(II) in 2. b) 1D hexagonal windows in 1–5 functionalized by different organic groups.

3.1. Screening of catalysts.

In our catalytic strategy, the acetylation of *p*-bromophenol and acetic anhydride in CH_2Cl_2 was chosen as a mode reaction to evaluated the catalytic activity of **1**–**5**, and the results are depicted in Fig.2. It can be seen from the plots that catalyst **2** yields the product almost quantitatively after 10 h, while the yields for catalysts **1**, **3**, **4** and **5** were lower than 97, 79, 78 and 74%, respectively. The results demonstrated that all the five PCPs display good catalytic efficiency toward the acetylation of phenols because both the coordinatively unsaturated Zn centers (similar to the previous literature²⁷) and the amide groups are introduces as trigger sites to achieve efficient guest interactions, a powerful catalytic driving force, and good signal responding communications, similar to the previous report.²⁶ Taken together, the acetylation of phenols were co-catalyzed by Zn Lewis acids and amide groups synergistically. However, the active differences found among the five PCPs cannot be attributed to the

differences in diffusion rate, because the five frameworks contained similar pore openings, but must be due to difference in the catalytic capacity of the active organic groups. Indeed, within the five PCPs, the coordinatively unsaturated Zn centers can be used as Lewis acid sites to activate reaction substrates, and the amide groups can behave as base-type catalytic driving force to promote the acetylation of phenols due to their two types of hydrogen bonding sites: the -NH moiety acts as an electron acceptor and the carbonyl group acts as an electron donor. It must be pointed out that, in 2, the pendent NH_2 groups present at the pore surface make 2 show a higher basicity than that of the other PCPs. Therefore, among the five zinc PCPs, -NH moiety in 2 can form the strongest hydrogen bond with phenol, resulting in an increase of the nucleophilicity of phenol, which is benefit for the completion of the acetylation reaction. The results can be explained by the early studies involving the deuterium isotope effect and kinetic investigations that intermolecular hydrogen bonds play a key role in the acetylation of phenols.²⁵ Accordingly, hydrogen-bonded phenols are better nucleophiles, and stronger hydrogen bonding results in more nucleophilicity and reactivity. Notably, the organization of the amide and amine groups in 2 may be precisely adjusted in such a way that they can behave synergistically as cooperative catalysts, similar to that of our previous report.²⁰ Together with the coordinatively unsaturated Zn centers and the strongest hydrogen bonding interaction among -CONH, $-NH_2$ and phenol, the compound 2 displays the highest catalytic activity among the five compounds, similar to that of the previous reports.²⁸⁻³⁰ Meanwhile, the lower activity of **5** might be ascribed to the decrease of base by the acid pendent COOH groups. Also, the activity observed for 2 catalyzed acetylation of phenols is superior to those found for [Zn(L)(NO₃)₂] (10 wt% loading, 98% yield and 24 h).³¹ Based on the above-mentioned fact, the following acetylation of phenols was explored by employing 2 as a heterogeneous catalyst.

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Fig. 2. Plots of yields versus time for the acetylation of p-bromophenol in CH₂Cl₂: comparison among the catalytic performance of 1–5.

3.2. The optimization of reaction parameters.

The optimization of the reaction conditions such as the effects of catalyst amount and solvents was carried out in a model acetylation system with 2 as the catalyst, and the results are collected in Table 1. The increase of the amount of catalyst from 1.0 to 3.0 mol% enhances the product yield from 80 to 99% but a further increase in the amount of catalyst leads to no significant increase in catalytic activity.

To select the most suitable solvent, experiments with various solvents (CH_2Cl_2 , THF, CH_3CN) and solvent-free have been carried out. Although the reaction was found to finish in neat acetic anhydride in 2 h, that in CH_2Cl_2 containing 3 equivalents of acetic anhydride was found to be complete in 10 h. The worst solvent is CH_3CN (80% yield) for 48 h.

Table 1. Optimization of parameters of acetylation of phenol catalyst 2.

OH	+	(CH ₃ CO) ₂ O	Catalyst r. t	
∖ Br				

entry	solvent	catalyst amount (mol%)	Time (h)	yield (%) ^a		
1	solvent-free	2	2	99		
2	dichloromethane	2	10	99		
3	tetrahydrofuran	2	48	83		
4	acetonitrile	2	48	80		
5	solvent-free	0%	6	4		
6	dichloromethane	1%	10	80		
7	dichloromethane	3%	10	99		
^a Yield of pure isolated product.						

3.3. The scope of acetylation of phenols

The remarkably simple and convenient reaction conditions, easy work up, and high yield for the transformation prompted us to extend the scope of 2 as heterogeneous catalyst for the acetylation of a wide variety of phenols. The results are summarized in Table 2. The results reveal that, the acetylation of various phenols proceeds in a facile manner to give the corresponding aryl acetates in quantitative yields except the acetylation of 4-phenylphenol. The substrates containing electron-withdrawing

groups were found to be acetylated faster than those containing electron-donating groups. For example, compared with the acetylation of *p*-bromophenol with *o*-nitro-*p*-methylphenol, the latter proceeds faster (10 h vs 8 h, entries 4 and 9, Table 2). This can be explained by the mechanism of acetylation of phenols. According to Bonner's studying,³² the *o*-nitro-*p*-methylphenol can form stronger hydrogen bond with acetic anhydride than that of *p*-bromophenol, and thus behaves as better nucleophiles for increasing reaction rate to achieve better product yield. Furthermore, in this catalytic system, a size-selectivity effect is also observed toward increasingly larger substrate sizes. For example, the conversion for *p*-phenylphenol with molecular dimension of 9.8 × 4.3 Å is reduced to 12% after 48 h (Table 2, entry 13). However, a small amount of pyridine is added the above system, which can promote the reaction to completion. When a larger substrate 2-isobutyl-4-phenylnaphthol is present, the reaction do not work under similar conditions (Table 2, entry 14). Since the pore sizes of **2** are 7.0 × 8.7 Å which exhibits the confined sizes and cavity, the largest substrate (9.9 × 10.0 Å) might be excluded in the catalyst due to difficulty in diffusion into the channels of **2**. This also suggests that the open active catalytic sites within the PCPs are not readily accessed by this particular substrate.

The assembly of the coordinatively unsaturated Zn centers and FOS into a robust PCPs can not only avoid their deactivations and but also create confined voids with high density of the accessible Lewis acid sites and active functional organic sites, resulting in a very efficient catalytic capacity that is not a simply linear sum of those of the pure components.

3.4. Control experiments

Considering the possibility of those ligands containing amide, or amine, or pyridyl groups to catalyze acetylation of phenols, performed control with we experiments N⁴,N⁴'-di(pyridin-4-yl)biphenyl-4,4'-dicarboxamide or 5-aminoisophthalic acid as catalysts instead of 2. As in the case of 2, the reaction of *p*-bromophenol with acetic anhydride in the presence of L or H₂aip afforded the same products with little lower yields under same reaction conditions (e.g., 20% for $H_{2}aip$, 76% for L vs 99% for 2). However, when L and $H_{2}aip$ were used as catalysts, all the acetylation reaction did not show any selectivity toward the reaction substrates. It is also noted that, the process involving 2 was heterogeneous, catalytic reaction in the presence of the two above-mentioned ligands was partially homogeneous, but without achieving complete dissolution of the two ligands. Therefore, compared to the two ligands, higher activity of 2 may be caused by much better accessibility of the catalyst's active sites. Taken together, these results indicate that the catalytic activity of 2 is superior to its corresponding components.

	он		0 O	
	R + (CH ₃ CC	D) ₂ O $\xrightarrow{\text{Catalyst 2 mol}\%}_{\text{CH}_2\text{Cl}_2, \text{ r. t}}$	R	
entry	substrate	moluclar size	time	yield ^a
1	ОН	0.65 nm 0.43 nm	14	99
2	OH	0.77 nm 0.43 nm	14	99
3	CI	0.61 nm 0.43 nm	12	99
4	Br	0.63 nm 0.43 nm	10	99
5	OH	0.55 nm	14	99
6	CI	0.55 nm 0.48 nm	14	99
7	CI	0.61 nm 0.55 nm	12	99
8	OH	0.75 nm 0.43 nm	16	99
9	OH NO ₂	0.56 nm	8	99
10	OH	0.69 nm (0.77 nm	18	99
11	НО	0.6 nm	24	98
12	OH	0.52 nm	24	98
13	ОН	0.98 nm 0.43 ni	m 48	12

Table 2. Acetylation of various phenols catalyzed by 2



3.5. Heterogeneity of 2

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To further verify whether 2 is a true heterogeneous catalyst or not, a procedure similar to that of our study and others was followed. We performed a controlled experiment, removed the catalyst by centrifugation, and the catalyst free solution was kept stirring under the same conditions and monitored by NMR analysis along the time to determine whether metal component dissolved from the solid structure of **2**. After removal of catalyst **2**, the conversion within 6 h only increased 2%, which could be attribute to the background reaction. The result confirms the assumption of a heterogeneous mechanism.

3.6. Recycle performance of 2.

Finally, in order to perform the catalyst recycling experiment, the used catalyst 2 (separated by filtration) was washed with ethyl acetate and dried at 80°C under vacuum. It was then reused for the acetylation of phenols as described above. The catalyst 2 was recycled in four consecutive experiments, and its activity remained essentially the same. As mentioned before, a corresponding product yield of 99% is achieved in the first run. In the second, third, and fourth run, the product yields, determined under the same conditions, decrease to 97%, 96%, and 94%, respectively. We have performed powder X-ray diffraction of catalyst 2 before and after the reaction and observed only a slight difference in peak after the reaction, as depicted in Fig. 3. These experiments are indicative that the frameworks essentially remains intact during the catalytic process. The recycle characterization and structural stabilities of other compounds are shown in Fig. S2-S5 (see ESI⁺ for details).



Fig. 3. XRD patterns of **2**: (a) the simulated XRD pattern, (b) the experimental one, (c) after the first recycling, (d) after the second recycling, and (e) after the fourth recycling.

Conclusions

In conclusion, all the PCPs **1–5** exhibit good size-selective catalysis for the acetylation of phenols. They effectively catalyzes the reaction of various phenols with acetic anhydride, and producing the corresponding phenyl acetates in excellent yields, depending on the nucleophile of the substrates. Among them, **2** is the most effective catalyst. Most importantly, the present study also provides further evidence that the porous coordination polymers with two different functionalities decorated the porous wall can be utilized as effective heterogeneous cooperative catalysts.

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