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The Role of Micropores and Amino Groups in Preferential CO₂ Adsorptivity of Porous Zn-Coordination Polymers Comprising Mixed Ligands of Triazole and Amino Triazole

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ABSTRACT

Porous coordination polymers (PCPs) of Zn²⁺, oxalic acid and mixture ratio of 3-amino, 1,2,4-triazole (ATaz) and 1,2,4-triazole (Taz) were synthesized to capture of carbon dioxide. A series of molar fraction Taz/(Taz + ATaz) prepared as 0.1;0.3;0.4;0.5;0.6;0.7 and 0.9 and also only ATaz and Taz ligand as 0 and 1 molar fraction respectively. Mixture of Taz and ATaz crystal induce new structure of 0.4, 0.5 and 0.6 molar fraction. Nitrogen adsorption of 50% mixture each ligand contribute the highest surface area as function of optimum condition to integrate pore space and amine group presence with adsorbed as 290 mgg⁻¹. This phenomena also shown through CO₂ adsorption amount as 135 mgg⁻¹, instead of 0.4, 0.6 and 0.7 molar fraction observed higher amount of CO₂ compared with only Taz ligand (X=1), indicate the integrated effects both of the ligand could generated the capture of higher amount of carbon dioxide.

Keywords: Mixed ligands, Amino triazole, Triazole, Adsorption, Carbon dioxide

INTRODUCTION

Porous coordination polymers (PCPs), are novel materials constructed by coordinate bonds between multi-dentate ligands and metal atoms became new attractive porous materials as highly selective gas adsorption capability.¹⁻⁶ Some of results have indicated that porous coordination polymers (PCPs) might become promising adsorbents for CO₂ separation.⁷⁻¹² Considerable effort has been

reported on the synthesis of PCP materials in the last several years. They are synthesized mainly by hydrothermal or solvothermal methods and the interesting synthesis of this material while choice of metal centers and design and synthesis of ligands. Different combinations of metal centers and ligands based on rational design ideas will generate PCP materials with various structures and preferential pore properties. Besides large surface areas and pore volumes, many PCP materials are well known



to have specific interaction of CO₂ with functionalized aromatic molecules has shown the effectiveness of introducing specific polar substituent groups, e.g. -OH, -COOH, -CH₃ or NH₂, on the aromatic ligand in increasing the CO₂-ligand affinity.^{13,14}

However, only a limited number of reports on frameworks having more than two kinds of ligands. Some of the reports about mixing ligand system was synthesized as Zn₄O(bdc)_x(abdc)_{3-x}, in which the terephthalic linkers are partially substituted by 2-aminobenzene-1,4-dicarboxylate (abdc). Otherwise, the potential of the mixed-ligand approach in the framework of Z₄O(L)₃ (L = terephthalic acid derivatives) was extended by use of a high-throughput technique.¹⁵ In the frameworks of the structure, various terephthalic acid derivatives can be incorporated to create a porous structure, and one of them has eight terephthalic acid derivatives in the crystal structure. They suggest that the matching of the interval of ligands and comparable strengths of coordination bonds are the key to integrating the different ligands in the structure.

Comprising of Zn²⁺, oxalic acid and 3-amino, 1,2,4-triazole was synthesized as flexible amine functionalized PCP.¹¹ These three dimensional frameworks built from the pillaring of Zn-aminotriazolate layers by the oxalate groups. The oxalate ligands bind to the zinc in a bidentate mode through two oxygen atom from different carboxylate groups. The aminotriazolate ligand bind to trigonal bipyramidal zinc centres through the three N-atoms of the ring, while the amino groups remain. This frameworks does not appear to be porous shown from did not show any appreciable uptake of N₂, Ar or H₂ under comparable condition. It possible because of presence of free amine groups inside the pore should blocked to penetrate of guest molecules. Interestingly, presence of amine groups create significant amount of carbon dioxide to capture in the frameworks. The potential of amine groups to interact with CO₂ molecules is by now reasonably well understood. In previously report, we have explored the new design of PCPs as Zn₂(C₂O₄)(C₂N₃H₂)₂·(H₂O)_{2.5} or Zn-oxac-Taz^{12,17} with triazole ligands with no amine groups presence which promoted significant N₂ amount adsorption isotherms and also available space to accept carbon dioxide molecules. If compare with others PCPs as Zn₂(C₂O₄)(C₂N₄H₃)₂·

(H₂O)_{0.511} or Zn-oxac-ATaz which have amine groups in ligands structure, no space observed for nitrogen adsorption isotherms even could capture CO₂ molecules due to their amine groups presence inside the pore interacted with CO₂ molecules.

In this study, we observed how PCPs were synthesized with two different properties of ligands could produce preferential framework of pore space and functional group combination effect in enhancing the CO₂ absorptivity. Herein, PCPs were synthesized to confirm the effects of amine groups interaction with CO₂ molecules by increasing pore space from 2 ligands of 1,2,4-Triazole (Taz) with no amine groups but create larger space were combined with 3-Amino, 1,2,4-Triazole (ataz) ligands with amine groups presence inside the pore. Mixture comparison of nTaz/n(Taz+ATaz) as 0.1, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.9 and to compare with ATaz and Taz ligand contain only, molar fraction mention as 0 for only ATaz ligand and 1 for only Taz ligand. Interesting phenomena observed by N₂ and CO₂ adsorption isotherms to give new flexibility pore properties of Porous Coordination Polymers (PCPs).

MATERIALS AND METHODS

Mixed ligand PCPs of 0.1 molar fraction was synthesized by 0.4 g of Zn₅(CO₃)₂(OH)₆ (Alfa Aesar, Co. Ltd.; 75% purity), 0.4 g of H₂C₂O₄ (Wako Pure Chemical Industries (WPCI), Ltd.), 0.14 g of 1,2,4-triazole (WPCI, Ltd.) and 1.44 g 3-amino, 1,2,4-triazole (WPCI, Ltd) were added to a mixed solution of 12 mL of methanol (WPCI, Ltd.; 99.5%) and 2 mL of distilled water. The solution containing white precipitates was transferred to PFA cell which was set in autoclave vessel and heated at 453 K for 12 hours. Then, cooling the system to room temperature, crystals prepared were filtered and washed with a mixture of methanol and water, followed by drying it at room temperature overnight.

The same procedure were used for synthesis of mixed ligands PCPs with molar fraction 0.3, 0.4, 0.5, 0.7 and 0.9 by variation change the weight of 1,2,4-triazole (Taz) and 3-amino, 1,2,4-triazole (ATaz).

Crystals prepared were characterized by a Rigaku X-ray diffractometer (XRD) Multiflex with

¹ Cu-K α at 40 kV and 20 mA and their morphologies were observed by using a JEOL scanning electron microscopy (SEM) JSM-7600 F. Thermogravimetric and differential thermal analyses (TG/DTA) were carried out using a Rigaku Thermo Plus TG8120. Samples enclosed in Al-pans were heated at 10 K/min from 298 to 723 K in air using Al₂O₃ as a reference.

¹ N₂ and CO₂ adsorption were measured at 77 and 303 K, respectively, by a custom-made volumetric adsorption system after each sample of Ca. 100 mg was pretreated at 333 K and 1 mPa for 1 h and then 383 K for 12 hours.

RESULTS AND DISCUSSION

Gradually increase of Taz ligand presence at 0.1 and 0.3 molar fraction shows only a slight change of XRD pattern, indicate no significant crystal structure changed or similar with only ATaz ligand (X=0). The same case for 0.7 and 0.9 molar fraction, XRD patterns almost similar with only Taz ligand presence (X=1). The mixture of Taz and ATaz crystal induced new structure of 0.4, 0.5 and 0.6 molar fraction as can be seen in Fig. 1. By using EXPO 201318, crystal system measured and only for X=0.1 molar fraction sample (only Taz ligand) formed as monoclinic crystal, then X=0 (ATaz), 0.1, and 0.3 as orthorhombic crystal system. Instead for 0.4, 0.5 and 0.6 molar fraction crystal formed as triclinic crystal system, similar to 0.7 and 0.9 molar fraction of Porous coordination polymers.

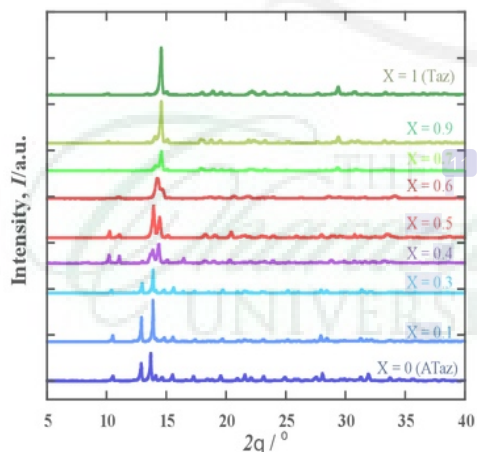


Fig. 1. XRD patterns of mixture ligands PCPs in various molar fraction

To confirm this crystal structure changes, SEM image also was observed in the same magnification and the specific phenomena shown in morphology properties (Fig. 2). Similar to XRD patterns, almost identical particle formed for 0, 0.1 and 0.3 molar fraction sample. Molar fraction sample of 0.9 and 1 also observed a similar morphology and a little bit different for 0.7 molar fraction sample, indicate the changed of peak intensity in XRD patterns make a slightly different of morphology. The completely different morphology observed in 0.4, 0.5, and 0.6 molar fraction samples. By using almost same comparison both of Taz and ATaz ligands induce the new structure and morphology to create integrating effects of pore space and amine group presences in the frameworks.

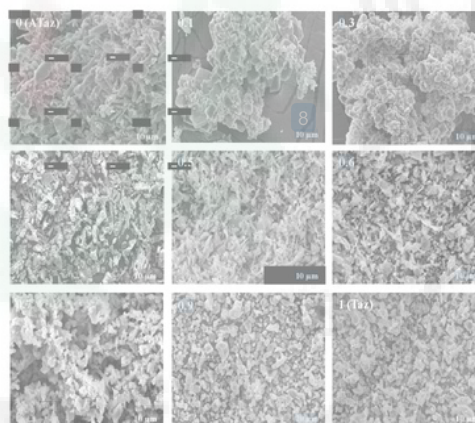


Fig. 2. SEM image of mixed ligand PCPs in various molar fraction

Figure 3 shows that pretreatment for 12 h before N₂ adsorption of PCPs with molar fraction 0.4, 0.5, 0.6, 0.7, 0.9 and 1 (Taz only) brought about significantly increased the adsorption amount from low pressure, whose adsorption isotherms are classified as type I. Presence more Taz ligands induce more space in the PCPs frameworks. On the other hand, PCPs with ATaz Ligands (X=0) and PCPs with molar fraction 0.1, 0.2 and 0.3 shows a pretreatment for 12 h brought about little change in the adsorption amount of N₂, but gradually increased at high pressure indicate presence of amine group block N₂ to penetrate inside the frameworks.

The new structure of 50% mixture ATaz and Taz ligand also bring out the high surface area and pore volume by nitrogen adsorption isotherms at 77K

as shown in Fig. 3, even though Zn-oxac-Taz ($X=1$) which no amine group has highest surface area, indicate more space formed with use ligands without amine group. In the other hand, nitrogen adsorption amount which almost no adsorption of nitrogen in 0.1 and 0.3 as similar with only ATaz ligand (0). Nitrogen could penetrate to the frameworks after 40% Taz ligand ($X=0.4$) exist, it suggest to create the pore space which enough for nitrogen molecules. And the surface area gradually decrease by presence of 10%, 30% and 40% ATaz ligand in framework for 0.9, 0.7 and 0.6 molar fraction respectively if compared to PCP with only Taz ligand ($X=1$). It confirm to presences of amine group inside the frameworks reduce the space of pores.

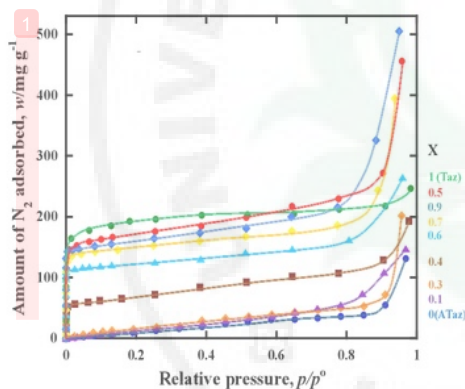


Fig. 3. N_2 adsorption isotherms of mixed ligand PCPs in various molar fraction at 77 K

Figure 4 shows the langmuir adsorption isotherms type through the integration effects of pore size and amine groups presences inside the frameworks more inexplicable by carbon dioxide adsorption isotherms. Even no nitrogen amount adsorbed in 0, 0.1 and 0.3 molar fraction crystal, significant amount of CO_2 can adsorbed which contribute from the CO_2 and $-NH_2$ interaction. And exist of 30% Taz ligand could make a little space and made CO_2 molecules can access to the pores, indicate by slightly increase of CO_2 adsorption amount. More interestingly, even 0.4, 0.6, 0.7 and 0.9 molar fraction crystal have lower adsorption amount of nitrogen if compared to PCP with only Taz ligand presence ($X=1$), indicate lower surface area or pore volume but could be adsorb higher CO_2 molecules. It confirm CO_2 and $-NH_2$ interaction have significant effects to increase CO_2 capacity inside the frameworks. Micropore volume,

BET Surface area and Langmuir surface area were summarized in Table 1 and Fig. 5. It clarified the effects of Taz ligand function act as pore space created which describe by nitrogen adsorption amount and amine group presence from ATaz ligand has big contribution to enhance the carbon dioxide adsorption amount. By increasing the surface area or provide bigger space inside the frameworks more effectives to enhance CO_2 amount indicated by higher amount of CO_2 adsorption over 0.4 molar fraction. Even though, the presence of an equal number of Taz and ATaz ligand become optimum condition not only to create the biggest surface area and pore volume but also the highest CO_2 molecules adsorb inside the frameworks.

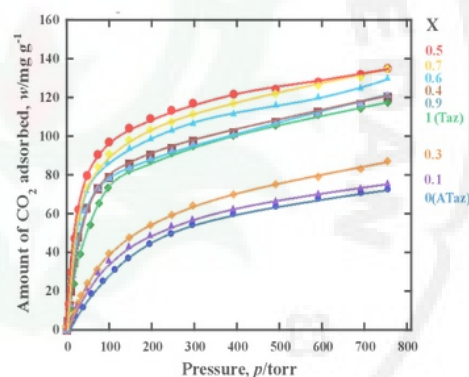


Fig. 4. CO_2 adsorption isotherms of mixed ligand PCPs in various molar fraction at 303 K.

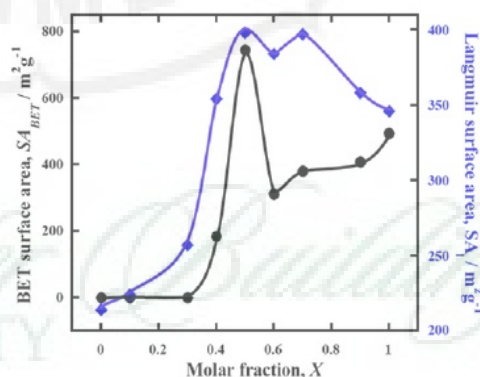


Fig. 5. BET surface area and Langmuir surface area all PCPs with various molar fraction

At a ratio of 50% ATaz and Taz ligand ($X=0.5$) induce the highest BET surface area is $544 \text{ m}^2 \text{ g}^{-1}$ due to the presence of amine ligands in the

cavity making a larger pore volume which caused by the interaction of the arrangement presence of amine groups in the pore supported by sufficient size of space from Taz ligand to make a larger cavity. BET surface area of PCP made from ligand comparisons X = 0 (Taz) to X=0.4 is smaller than X = 0.6 to X=1 (ATaz), which indicate the presence of more amine

groups were blocked nitrogen gas to penetrate inside the pores. Decrease of the number of amine groups increases the BET surface area in PCPs with molar fraction, X = 0.6 - 1 (ATaz) although lower than the PCP made with the same ratio or X = 0.5. It confirmed the pore size formed by the presence of 50% ligand ATaz and Taz due to this flexible structure of these PCPs series.^{11,12,17}

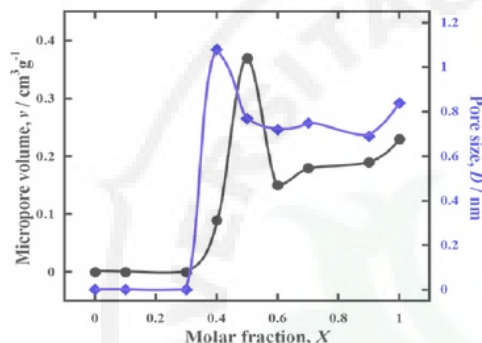


Fig. 6. Pore size and micropore volume all PCPs with various molar fraction

It is also observed in the Langmuir surface area, CO₂ was absorbed at larger pore sizes with the presence of amine groups in the pore. However, despite the pore volume of 0.37 cm³g⁻¹ formed in PCP with a ligand ratio of X = 0.5, the largest pore size was observed in PCP with a ligand ratio of X = 0.4 as 1.08 nm. (Fig. 6). Almost no pore formed in PCPs were synthesized from a mixture of ligands with a molar fraction of 0(ATaz) to X=0.3 because the presence of amine groups still blocked the pores from the guest molecule interpenetrate. PCPs were synthesized of Taz/ATaz 0.4 molar fraction, induce to maximum pore size formation, then PCP

Table 1: Summary of gas adsorption data. was formed by a molar fraction of 0.5 has a larger pore volume. It suggest how flexible the PCP structure is easily to be modified by comparison of ligand composition

Molar Fraction	CO ₂ adsorption			N ₂ adsorption			
	adsorbed amount at 100 torr (mg g ⁻¹)	adsorbed amount at 700 torr (mg g ⁻¹)	SA _{Lang} (m ² g ⁻¹)	adsorbed amount at 0.1 P/Po	Micropore Volume (cm ³ g ⁻¹)	Pore Size *D (nm)	SA _{BET} (m ² g ⁻¹)
0 (ATaz)	31.3	72.8	214	6.6	-	-	-
0.1	33.3	77.8	224	8.5	-	-	-
0.3	39.5	87.2	257	10.9	-	-	-
0.4	78.8	120.3	354	65.6	0.09	1.08	185
0.5	97.1	135	398	290.1	0.37	0.77	544
0.6	86.9	130.3	384	120.3	0.15	0.72	311
0.7	90.9	134.8	397	145.0	0.18	0.75	380
0.9	78.7	121.7	358	155.0	0.19	0.69	408
1 (Taz)	73.4	117.4	346	185.2	0.23	0.84	494

*micropore volume estimated by DR plot analysis and pore size by t-plot analysis of N₂ adsorption isotherms at 77K.

CONCLUSION

A series of new PCP design from mixture ATaz and Taz ligand can explain how strong the amine groups interaction with carbon dioxide through bigger pore space needed to allow carbon dioxide molecule through inside the pores. By increasing the surface area from Taz ligand and presence of amine groups up to 60% from ATaz ligand more effective to increase to capture the CO₂ molecules. PCPs prepared in 50% contain both of ligand shown

the best composition to get the highest not only surface area, but also the carbon dioxide capacity. It become the new strategy to prepare PCP which have preferential properties for CO₂ adsorption.

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