

Synthesis, XANES/EXAFS Fine Structure Characterization, and N₂/CO₂ Adsorptive Selectivity of Cobalt-based Metal Azolate Frameworks

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Abstract

One of the best gas adsorptive/separated materials is metal azolate frameworks (MAFs) due to its excellent stability and active interaction with gases. In this study, all MAFs were synthesized by green processes including aqueous solution mixing and acid catalyzed method.

Crystal structures and morphologies of cobalt-based metal azolate frameworks (MAFs) were confirmed by XRD and FE-SEM respectively. Furthermore, FTIR and TGA analyses were also used for investigation of bonding phenomenon and thermal stabilities. Valent of Co atom and their bond distances in cobalt MAFs were investigated by XANES and EXAFS. The Co atoms in ZIF-67 and dia-Co(mim)₂ existed by two oxidation states (Co²⁺ and Co³⁺). Bond distance of Co-O in ZIF-67 and dia-Co(mim)₂ were 1.3 and 1.5 Å respectively. The BET surface area, N₂, and CO₂ adsorption amount of MAFs were measured by micrometrics ASAP 2020. N₂ adsorption curves of ZIF-67 and dia-Co(mim)₂ (mim: 2-methylimidazole) were Type I and Type III. In addition, the pore arrangement of ZIF-67 and dia-Co(mim)₂ could be identified by comparing the N₂ adsorption curves to IUPAC standard patterns that displayed cylinder and slit-plane arrangement respectively. These result revealed that synthesized cobalt MAFs had the highly potential to separate CO₂ from mixed gases for the industrial air pollution control application.

Keywords: CO₂ capture, Cobalt-based MAFs, Green synthesis method, XANES/EXAFS, N₂/CO₂ adsorptive separation.

1 Introduction

Fuel consumption is rising with industrialization procedure, and almost 85% energy is providing by fossil fuels like coal, petroleum, and nature gas. This causes green house gases (GHG) emission and concentration increasing resulting in climate change [1]. Furthermore, industrial emission gases almost belong with multicomponent gas mixture, which composed of CO₂, O₂, H₂, olefin, paraffin, C₈ alkyl-aromatic isomers, aliphatic isomers, and hydrocarbon [2]. In order to utilize these gases in industrial off-gas, gas separation and purification technologies become a popular field for scientists.

Porous materials which can be made into particle absorbent and thin membrane are the best option for gas separation and storage because it can satisfy the operation conditions of gas drying, air separation, synthesis gas production and carbon dioxide capture that are the most required processes in industry [3]. Compared with other porous materials (zeolite, metal-oxide sieve, aluminophosphates, activated carbon, activated alumina, silica gel, pillared clays, inorganic resin, porous metal organic composites), metal azolate frameworks (MAFs) are the most potential material for gas separation due to its excellent structure tunability, high surface area and good gas adsorption ability [4].

MAFs, metal organic frameworks (MOFs) and zeolite imidazolate frameworks (ZIFs) are porous materials which composed by transitional metal ions and organic ligands with three-dimension structures (**Figure 1**). But M-Im-M angle in MAFs and ZIFs are similar to Si-O-Si angle (145°) which lead to the synthesis of MAFs with zeolite-type tetrahedral topologies [5]. The main body of imidazole and

its derivations are azole which is a heterocyclic ring with nitrogen atoms, and it is used for medicine, agriculture, industry and coordination chemistry fields widely. MAFs have good structure tunability owing to excellent electron transportation between metal ions and N atoms in whole structure.

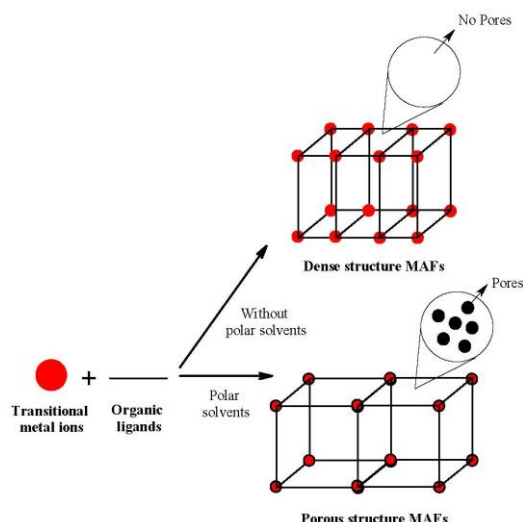
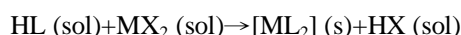


Figure 1 Schematic presentation of the MAFs constructed by transitional metal ions and organic ligands.

Preparation reactions of MAFs which include solvent, base solvent, electrochemistry, mechanochemistry (grinding), and non-solvent (aqueous solution mixing), and acid-base neutralization methods are common methods nowadays (**Table 1**). And their chemical reactions are showed below [6][7]:

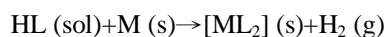
(1) Solvent method:



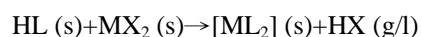
(2) Base solvent method:



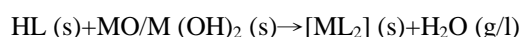
(3) Electrochemistry (EC):



(4) Mechanochemistry (MC):



(5) Non-solvent method :



(6) Acid-base neutralization method (ABN):



HL=Acidic ligand, M=Metal, X=Counter anion

Table 1 Comparison between several main cobalt-based MAFs synthesis reactions.

Reaction	Energy consumption	Yield	Byproduct	Industrial scale /Environment friendly?
Solvent Base solvent	Medium	Low - Medium	Soluble salts, water and ions	Yes/No
EC	High	Medium - High	Hydrogen	No/Yes
MC	Low	Low - Medium	Soluble salts, water and ions	Yes/Yes
Non-solvent ABN	Low	Medium - High	Water	Yes/Yes

(1), (2) are the reactions which need huge amount of organic solvents as a reaction-catalyzing or structure-directing agent among these synthesis methods so as to form or transform the non-porous cobalt-based MAFs into porous structure. Both of them produce many byproducts (organic solvent and soluble salts) that are not only lower product (MAFs) yield but also cause environmental pollution. Although (3) can prevents the problems of (1) and (2), the inflammable H_2 is dangerous during this reaction [8],[9]. Reactants in (4) are solid phase, but it still generates some byproducts that can only use acid solvent to wash it out [10][12]. (5) and (6) are the most ideal choices among all reactions because their reactants (metal oxide/metal hydrate) and byproducts (water) are cheap, nontoxic, and recyclable for industrial manufacturing processes [6]. Their synthesis operation is also easy to operate by solution mixing simply.

However, cobalt-based MAFs will tend to form non-porous dense structure without organic solvent as structure-directing agent [13]. For this reason, reactant molar concentrations and polar solvent treatments become important variables for porous MAFs preparation in aqueous solution. And the gas adsorption-desorption behavior of non-porous cobalt-based MAFs are always ignored because of its low surface area and poor gas activation. This study will focus on the comparisons of gas adsorption-desorption behavior between high and low surface area of cobalt-based MAFs in order to find the inert

gas separation materials with chemical and thermal stability dense structure.

2 Experimental

2.1 Materials

Cobalt oxide with purity 99.0 % were purchased from Alfa Aesar. Imidazole and 2-methylimidazole were purchased from J.T. Baker and Aldrich. Acetic acid and ethanol were purchased from Merck. All reactants were commercially available and used without further purification.

2.2 Synthesis of cobalt-based MAFs

Acid-catalyzed and non-solvent method could make dense and porous cobalt-based MAFs respectively. The details of both reactions were showed in **Figure 2**. and **Figure 3**. Crystal structure and morphology of some cobalt-based MAFs were much different although they were made from the same reactants.

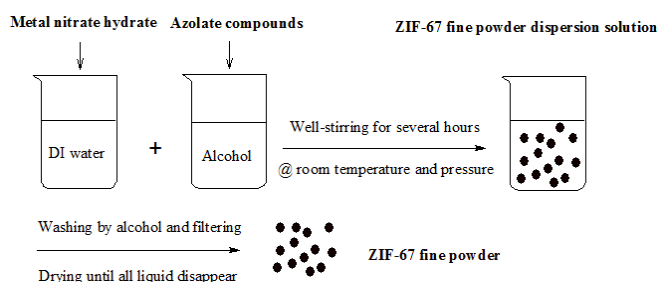


Figure 2 Synthesis procedure of ZIF-67.

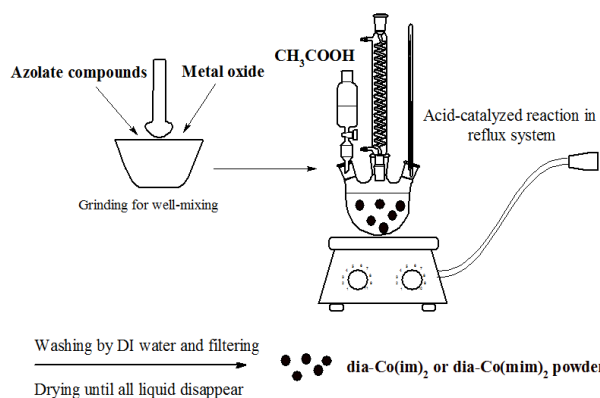


Figure 3 Synthesis procedure of dia-Co(im)₂ and dia-Co(mim)₂.

3 Results and Discussion

3.1 Crystal structure investigation

XRD patterns of as-synthesized cobalt-based MAFs are showed in **Figure 4**. All cobalt-based MAFs are synthesized successfully and the XRD patterns are well match with their standard patterns in literature. However, two of them (**Figure 4(a)**) slightly shifted to left because of the uniform stress during the grinding process. High intensities and sharp peaks in XRD patterns reveal good crystallization of cobalt-based MAFs. Morphologies of cobalt-based MAFs are observed by FE-SEM. Crystal surface of dense cobalt-based MAFs are smooth, and their grain size are larger than porous cobalt-based MAFs. Overall, crystal shapes of dense and porous cobalt-based MAFs are tetragon and polyhedron, respectively. Certainly, existence of structure-directing agents in solution is an important factor which affects the crystal structure transformation significantly.

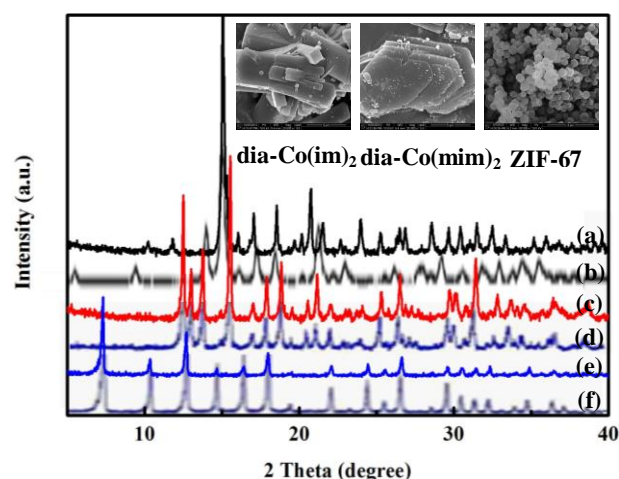


Figure 4 XRD patterns of (a) dia-Co(im)₂, (b) dia-Co(im)₂ [14], (c) dia-Co(mim)₂, (d) dia-Co(mim)₂ [15], (e) ZIF-67 and (f) ZIF-67 [15] (FE-SEM micro photos at magnification 30,000 were showed above XRD patterns).

3.2 Bonding between atoms in MAFs

Tran et al [16]. contrasted FTIR spectra of ZIF-8 with 2-methylimidazole in wavenumber 3400cm⁻¹ - 2200cm⁻¹ during the preparation of ZIF-8. They discovered signal intensity of N-H...H in 2-methylimidazole decreasing at 2600cm⁻¹ as a result of N atoms in heterocycle become deprotonated and then bonded to metal ions through whole reaction. Consequently, we could judge whether the bonding between imidazolates and metal ions formed or not by measuring the intensity between wavenumber 3400cm⁻¹-2600cm⁻¹ region. This result provided a method

with easy and convenient judgment. **Figure 5** showed significant decreasing at 2600 cm^{-1} that hinted the bonding between N atom (in heterocycle) and metal ion.

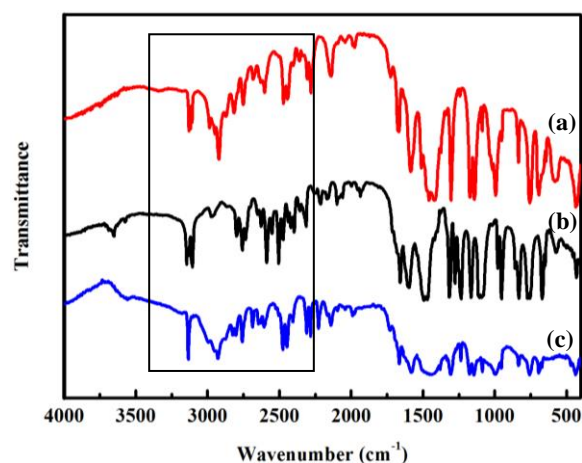


Figure 5 FTIR transmittance spectra of cobalt MAFs of (a) dia- Co(im)₂, (b) dia-Co(mim)₂ and (c) ZIF-67.

XANES and EXAFS spectra were used to investigate the valent and bond distance of cobalt metal atom respectively. Valent of cobalt atom in cobalt-based MAFs were showed in **Figure 6**. Cobalt ion in ZIF-67 and dia-Co(mim)₂ existed by Co²⁺ and Co^{+2.5} state after comparing with other cobalt standards. To evaluate the bond distance between cobalt and its neighbor oxygen atom, EXAFS spectra was introduced to do this work. **Figure 7** were the EXAFS spectra of cobalt standards and cobalt-based MAFs. After modeling fitting by cobalt oxide (CoO), the Co-O bond distance of ZIF-67 and dia-Co(mim)₂ were 1.3 and 1.5 Å respectively.

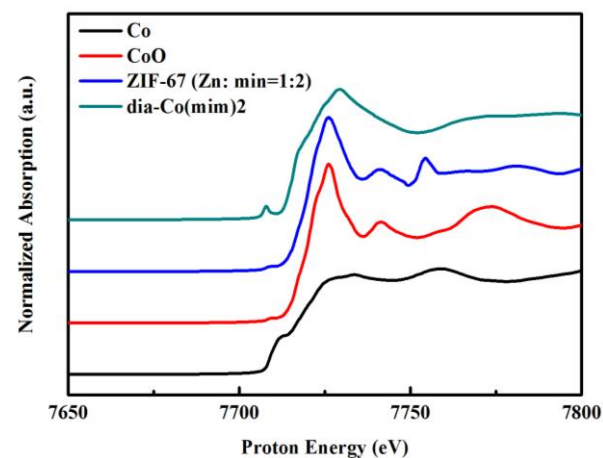


Figure 6 XANES spectra of cobalt-based standards and MAFs.

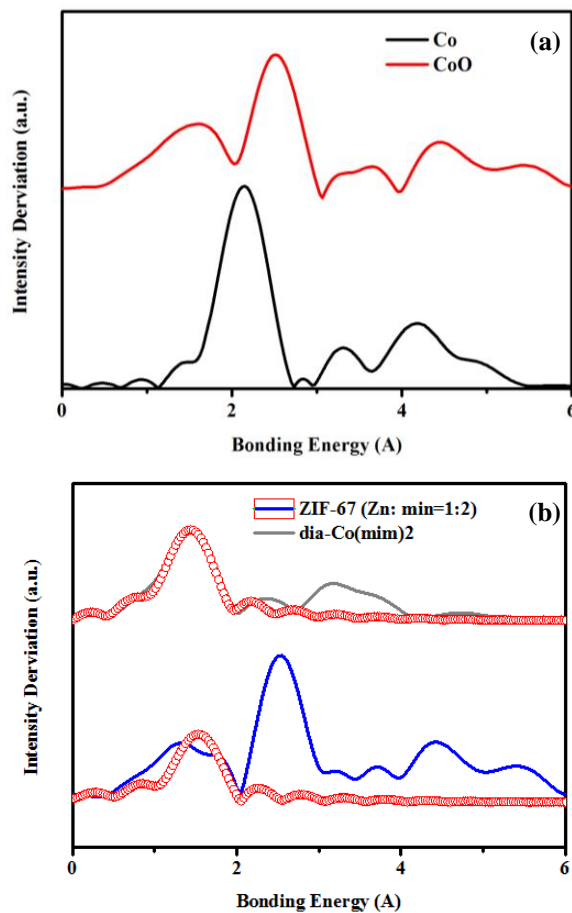


Figure 7 EXAFS spectra of (a) cobalt standards and (b) cobalt-based MAFs.

3.3 N₂ and CO₂ adsorptive selectivity of MAFs

Surface area and pore size distribution of cobalt-based MAFs could be calculated from N₂ adsorption-desorption isotherms shown in **Figure 8** (a). Dense and porous cobalt-based MAFs were classified as Type III and Type I according to the IUPAC standard isotherms respectively. Type I always appeared on microporous material, all adsorbed gas molecules were filled in internal pores approaching relative pressure $\ll 1$. Adsorption isotherms raise immediately at saturated pressures whose phenomenon was similar with macroporous adsorption because of there had interstices between each particle. Besides, Type III occurred when interaction between solid surface and adsorbent was poor. And no B point (transitional point) in isotherms meant that the behavior was multilayer adsorption. The surface area, pore size distribution and saturated N₂/CO₂ adsorption amount were summarized in **Table 2**.

In spite of the surface area and N_2 adsorption amount of $zni-Zn(im)_2$ and $dia-Co(im)_2$ were much lower than porous cobalt-based MAFs in this study, their CO_2 amount were higher than others before 395 and 200 mmHg respectively (**Figure 8** (b)). It was caused by crystal structure (organic ligand length), gas activation and interaction strength between cobalt-based MAFs surface and gas molecules. From the chemical viewpoint, long and branched molecular chains had more opportunity of aggregating and then formed a dense structure if there had no polar solvent as structure-directing agent. This aggregation also lowered cobalt-based MAFs effective adsorption surface area and decreased the activation and interaction strength between cobalt-based MAFs surface and gas molecules. Therefore, it was important to choose the proper organic ligand preventing aggregation and polar solvent being structure-directing agent.

Table 2 Surface area, pore aperture distribution percentages and gases adsorbed amounts of cobalt-based MAFs (dia: diamond, sat: saturated).

Components	S_{BET} (m^2/g)	Pore size distribution		Sat. N_2/CO_2 volume adsorbed (cm^3/g STP)
		V_{micro} (%)	V_{meso} (%)	
$dia-Co(im)_2$	2.00	2.9	0.0	4.45/16.18
$dia-Co(mim)_2$	17.4	26.0	3.6	27.35/2.71
ZIF-67	1241.6	94.5	5.5	452.40/41.35

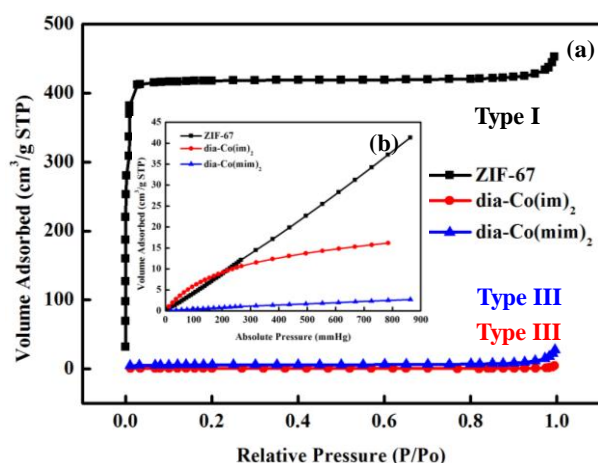


Figure 8 (a) N_2 and (b) CO_2 adsorption isotherms of as-synthesized cobalt-based MAFs.

4 Conclusion

All cobalt-based MAFs were prepared by green and environment-friendly synthesis methods named acid-catalyzed and non-solvent methods successfully that were proofed by XRD, FE-SEM and FTIR. ZIF-67 was porous materials with higher N_2 and CO_2 adsorption capacity, but other dense cobalt-based MAFs were contrary to it according to gas adsorption isotherms. However, $dia-Co(im)_2$ still had potential for gas separation which displayed good adsorption ability in CO_2 isotherms. Gas adsorption capacity was highly related surface area, pore size/arrangement and activation. In adsorption isotherms, $dia-Co(im)_2$ was dense structure with good activation to CO_2 . They can play an important role for N_2/CO_2 separation.

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