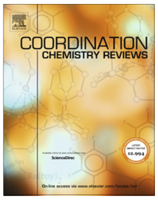
Coordination Chemistry Reviews 365 (2018) 1–22

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Synthetic approaches for the incorporation of free amine functionalities in porous coordination polymers for enhanced CO_2 sorption

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ARTICLE INFO

Article history:
Received 16 December 2017
Received in revised form 13 February 2018
Accepted 19 February 2018

Keywords:
Coordination polymer
Metal-organic frameworks (MOFs)
Carbon dioxide
Porous materials

ABSTRACT

Porous coordination polymers, or metal–organic frameworks (MOFs), provide a unique materials platform due to their regular structure that allows for almost unlimited tunability in terms of pore size, shape, dimensionality and chemical functionalisation. The ability of this class of material to act as agents for the selective capture or separation of small molecules has driven much of the research in the field over the past two decades.

One of the major driving forces in recent years has been the ability of porous coordination polymers to act as selective hosts for carbon dioxide, with obvious potential environmental implications for successful materials. Efforts to enhance the selectivity for CO_2 over other gases (particularly those present in exhaust flues) have explored chemical functionalisation of the interior pore space using amines, to give materials that to some extent mimic the standard solution-based processing methods of flue gas that are currently employed.

This review examines the three major synthetic routes that are used in order to affect this chemical modification of porous frameworks; (i) post-synthetic grafting of amines to coordinatively unsaturated metal sites, (ii) incorporation of ligands that contain terminal amine groups, and (iii) incorporation of ligands that contain amine embedded within the core of the ligand. The relative merits and shortcomings of these different synthetic approaches are discussed alongside examples of the materials generated using each method.

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https://doi.org/10.1016/j.ccr.2018.02.012

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1. Introduction

Porous coordination polymers, or metal–organic frameworks (MOFs), are a well-known class of materials in which organic linkers are used to bridge between metal ions (or clusters thereof) resulting in a usable internal pore space [1–3]. In their first report of a designed coordination scaffold, Hoskins and Robson declared that “they may show interesting molecular sieve and ion exchange properties, they may have unusual mechanical and electrical properties, and they may, after appropriate functionalization of the rods, provide tailor-made materials for the heterogeneous catalysis of a wide range of transformations”, and over the intervening decades this prophetic statement has been continuously fulfilled [4]. The ability to design and tailor these materials, especially in terms of pore size and chemical functionalisation, provides boundless synthetic opportunities and the possibility for numerous applications [5].

One potential application of porous coordination polymers which has dominated research efforts over the past decade is sorption and/or separation of CO_2 and other gases [6–8]. With global recognition of carbon dioxide as a major influence on worldwide climate patterns, there is an intense push for new technologies that are capable of removing carbon dioxide from flue gas streams and even from the atmosphere [9,10]. Current methods rely on aqueous amines for chemical scrubbing of exhaust gases from coal-fired power plants and other industrial vents [11]. There are many issues associated with this method, most notably the huge power costs of regenerating the free amines (calculated to be 30% of the power actually generated) [12,13]. These amine solutions, typically involving monoethanolamine (mea), are also very corrosive, hazardous and prone to decomposition, meaning that moving to a viable heterogeneous method, or the use of other technologies, is highly desirable [14–17]. The choice of amine is important; for example, secondary amines have been reported to give accelerated the rates of sorption and desorption, which has been shown industrially for alkanolamines (piperazine in particular) [18,19].

The uptake of CO_2 by a wide variety of porous coordination polymers, and other solid sorbents, has been reported and the topic has been reviewed on several occasions [20–22]. Generally, the vast majority of these materials are able to adsorb CO_2 with little effort when placed in a pure atmosphere of the gas (the empty pore spaces fill readily when evacuated) and show selectivity for CO_2 over many other gases due to its polarity. The challenge is to design materials with specific sites for physical or chemical interaction with CO_2 that enhances binding above that observed for the average porous material [23]. These functional sites may be vacant metal coordination sites, Lewis or Brønsted acidic sites, charged functionalities and others which have been reviewed elsewhere [24,25]. For example, the NOTT-300 framework has shown very high CO_2 selectivity by utilisation of a hydroxyl-lined pore space [26]. However, the functionality that has received more attention than any other is the amine group [27]. The use of amine functionalities within the pores of porous coordination polymers provides polar sites that have the ability to interact strongly with CO_2 and that have the potential to mimic the behaviour of the aqueous amine solutions that are currently used which form carbamates in solution (Fig. 1) [28].

In the context of porous coordination polymers, the effect of amines on CO_2 adsorption has been computationally studies in order to explore the interactions between CO_2 and a range of aliphatic and aromatic amine ligands [29]. This study showed binding energies ranges from 8.8 kJ/mol for the aromatic amine 2-aminoterephthalate to 17 kJ/mol for the tertiary amine 4-dimethy laminomethylene-1,2,3-triazole-1-phenyl. In addition, the CO_2 affinity of aliphatic amines was confirmed, using cluster calculations, to be higher than that of aromatic amines due to their greater basicity. It has also been shown that stronger CO_2 interactions are found for nitrogen-containing heteroaromatics compared to standard building blocks, with amine-functionalised units and azo-bridged ligands also being good candidates for stronger CO_2 binding [30]. In addition to their application for CO_2 sorption, amine-based coordination polymers have also been used as heterogeneous Lewis basic catalysts, for example, in Knoevenagel condensations (see later).

In terms of carbon dioxide capture, particularly with relevance to removal of CO_2 from flue streams which are *ca.* 10% H_2O, the water stability of the framework and the chemical behaviour of the amines in moist environments is important. A detailed discussion of stability is outside the scope of this article, but has been comprehensively reviewed by others [31–33]. In general the presence of moisture has a negative impact on CO_2 sorption, even if the framework itself remains structurally intact, although this is not always the case. For instance, small amounts of moisture in HKUST-1 enhance CO_2 sorption (due to increased electrostatic interactions from H_2O occupying vacant coordination sites), yet high loadings significantly decrease uptake [34,35]. Mg–MOF-74, which also relies on vacant coordination sites for its activity, shows reduction of CO_2 capacity at all levels of water loading [36]. MIL-100(Fe) demonstrates a fivefold increase in breakthrough capacity at low pressures through enhanced solubilisation of CO_2 within the pore space, highlighting that the effects of hydration are not always negative [37]. Water not only affects the performance of porous materials, in can influence the nature of the interaction of CO_2 with amine-containing ligands. A recent report details how IRMOF-74-III–$(CH_2NH_2)_2$ (a derivative of the $[Mg_2(dobdc)]$ series, containing a bis-methylamine substituted *p*-terphenyl linker, see Section 3.4) forms different reaction products within the pore space depending on the presence of water vapour [38]. In dry conditions CO_2 interacts with the methylamine sites to form a carbamic acid, whereas when the material is exposed to 95% relative humidity before CO_2 loading the adsorbed species is identified as ammonium carbonate.

There are different synthetic approaches by which amine functionalities can be incorporated into porous coordination polymers. This review article aims to explore examples of each of these approaches and highlight the benefits and pitfalls of each. The synthetic routes can be broadly categorised into three areas: (i) post-synthetically ‘grafting’ amines onto vacant metal coordination sites, (ii) using ligands that have (typically aromatic) pendant amines covalently attached, and (iii) using ligands in which the amines are embedded within the main backbone of the bridging ligands (Fig. 2). This review article is intended to cover the main synthetic strategies, as outlined above, that have been reported for the incorporation of amines into porous coordination polymers and to give an overview of the general principles, rather than a comprehensive and in-depth treatment of each individual approach. The advantages and disadvantages of each approach are highlighted, alongside pertinent examples and recent developments.