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Review

Design strategies for metal-organic frameworks selectively capturing harmful gases

Ki Chul Kim

Department of Chemical Engineering, Konkuk University, Seoul 05029, Republic of Korea

A R T I C L E I N F O

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A B S T R A C T

Metal-organic frameworks (MOFs) have attracted a special attention to the selective capture of harmful gases from air, owing to the presence of a high density of active surfaces that can be tailored by an appropriate modification. In this paper, recent studies on appropriate approaches for the selective capture of harmful gases (NH_3, CO, H_2S, NO*x*, SO*x*, Cl_2, etc.) performed *via* experimental and computational methods are comprehensively reviewed with the aim of establishing well-designed strategies for the specific tasks. Three primary conclusions regarding the design strategy of MOFs are highlighted from the reviewed studies: the introduction of appropriate open metal sites for the selective capture of polar harmful gases, inefficiency of open metal sites introduced for the selective capture of non-polar harmful gases, and introduction of appropriate surface functionality for individual harmful gas. It is believed that the review will play a critical role in designing promising MOFs with appropriate surface chemistry for the selective capture of harmful gases from air.

Contents

1. Introduction

Global demand on the petrochemicals and carbon-based energy resources has increased with the rapid increase of the global population and explosive growth of the industrialization all over the countries [1]. Currently, the global energy demand of approximately 85% is supported by burning fossil fuels such as coal, petroleum, and natural gas [2]. Coal-fired power plants are a representative type of power generation station that can make use of the combustion of coal to provide around 40% of the world's electricity [3,4]. However, the use of the coal produces a large amount of various pollutants such as CO_2, carbon monoxide, sulfur dioxide, and NO*x*, reducing air quality and affecting climate change. Concerns about the environmental impact caused by the increase of the harmful gases in the atmosphere prompt the need to find an alternative clean and renewable energy resources [5–14]. A variety of carbon-free sustainable energy resources such as solar [5–8], wind [8–10], wave [11,12], and geothermal energies [13,14], have been proposed as promising candidates from studies that have focused on finding environmentally benign energy resources. However, despite such rigorous efforts, none of them stably provides sufficient amount of energy resources in a safe way. The supplies of the solar and wind energies depend on weather conditions while the geothermal energy is harnessed from hot rocks within Earth's crust, making it dependent of location. Thus, it is necessary to keep the concentrations of harmful gases evolved from fossil fuels at a safe level until the renewable energy resources

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E-mail address: kich2018@konkuk.ac.kr.

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become mature enough to replace the fossil fuels. For example, efficient carbon capture and sequestration (CCS) technologies need to deployed to reduce CO_2 emissions, particularly in the stationary point sources such as the coal-fired power plants, which account for approximately 60% of the total emission in the world [1,4]. In addition to the harmful gases produced from the fossil fuels, ammonia produced from the nitrogenous animal and vegetable matter is another harmful gas that can found in trace quantities in nature. Since ammonia is a severe irritant to the eyes, nose, throat, and lungs, it is a potential hazard to be removed from air.

Significant efforts have been made to selectively capture harmful gases from air [15–22]. Chemical absorption has been proposed as an approach to efficiently capture the harmful gases [15–22]. Wet amine scrubbing method such as monoethanolamine (MEA) in aqueous solutions is a typical approach involving chemical absorption of CO_2 by amine solutions [15–18]. The CO_2 removal by absorbing and stripping with aqueous amine is a well-established technology [16–18]. Nitrogen-containing organic compounds such as N-functionalized imidazoles are used to control emissions of sulfur dioxide, the main contributor to acid rain, and thus maintain the air quality at a low level [19]. Dilute sulfuric acid is typically used as an ammonia scrubber to neutralize ammonia through the chemical absorption. However, there are several drawbacks in the chemical absorption approach: the high energy consumption to regenerate the utilized absorbent solutions and solvent loss arising from the solution evaporation [15,18]. Although amine-functionalized ionic liquids have attracted much attention as a method to alleviate the problem of the solution evaporation, it is still needed to lower its regeneration energy [20–22].

Recently, physical adsorption performed by solid adsorbents such as porous carbon materials [23–25], zeolites [26–31], and metal-organic frameworks (MOFs) [32–35] has emerged to be another promising approach that can overcome the major challenges of the chemical absorption approach minimizing the loss of their performance of selectively capturing harmful gases. The solid adsorbents are free from the high energy consumption for the regeneration processes and possibility of high equipment corrosions [36,37]. Among the solid adsorbent candidates, MOFs, namely extended crystalline porous materials where metal cations or their oxide clusters are connected by multitopic organic linkers, have attracted special attention due to their superior ability for the physical adsorption arising from the following benefits: large internal surface areas and extensive porosity as well as relatively flexible tunability of surface chemistry as compared with other porous materials and infinite number of possible combinations afforded by the variety of metal nodes, organic linkers, and structural topologies [32–35]. All these benefits have enabled MOFs to be fully utilized for various applications including the harmful gas capture. However, despite such rapidly growing importance on MOFs for harmful gas capture applications, most of research articles have been focused on applications for the CO_2 capture. This has led to a limited understanding on the potential of MOFs for non-CO_2 capture applications. Hence, it is necessary to make a comprehensive review on this issue.

In this paper, a variety of studies on MOFs that have been employed for selectively capturing various non-CO_2 harmful gases including NH_3, CO, H_2S, NO_x, SO_x, Cl_2, and Br_2 are concisely and comprehensively reviewed with the aim of developing design strategies of MOFs with optimal performance. The review is primarily focused on evaluating various MOFs with a selected set of performance factors to identify common rules that would lead to the design of MOFs with optimal performance for the selective harmful gas capture under humid conditions. Review articles on the utilization of MOFs for CCS can be found elsewhere [35,38–43]. The introduction is followed by a critical review of various studies of MOFs for the aforementioned applications.

2. Capture of harmful gases other than carbon dioxide

As stated early, ammonia is a potential hazard that can severely irritate the eyes, nose, throat, and lung so that it should be removed from air. OSHA has a guideline regarding exposure limits for ammonia such as a 15 min exposure limit of 35 ppm for ammonia and an 8 h exposure limit of 25 ppm for ammonia [44]. Likewise, NO*x* is a general term for nitrogen oxides such as nitric oxide and nitrogen dioxide in air pollution that possibly contribute to the formation of smog and acid rain. NO*x* gases are commonly generated from internal combustion engine exhaust and power station boilers. Carbon monoxide that is typically formed by burning carbon-based fuels is an odorless, colorless, toxic gas that prevents the ability of our bodies from transporting oxygen to all parts of the body. Hydrogen sulfide is a colorless, poisonous, flammable gas with the odor of rotten eggs that can cause the microbial breakdown of organic matter in the absence of oxygen gas in our body. Hydrogen sulfide is commonly found as an impurity in the petroleum and natural gas industries and used as a reagent in a vast number of industrial processes. Exposure to chlorine beyond a threshold limit value can poison our body with respiratory problems such as difficulty breathing. Besides, information on other harmful gases have been collected and reported according to the level of the toxicity [45]. Primarily assisted by MOFs, significant efforts have been made to selectively capture such harmful gases from air in a hazardous situation and thus alleviate the environmental risks and health problems.

Incorporation of coordinatively unsaturated open metal sites in either metallic centers or organic ligands for MOFs has been introduced as a primary approach to capture non-CO_2 harmful gases. A variety of MOFs with open metal sites including the two representative MOFs, namely M-MOF-74 and Cu-BTC, applied to the selective CO_2 capture have been utilized to selectively capture the non-CO_2 harmful gases [46–51]. It is clear that the open metal sites tend to be Lew acidic and thus highly effective as strong adsorption sites for harmful gases that can act as Lewis bases. For instance, Morris and coworkers observed nitric oxide (NO) molecules that could strongly bind empty copper metal sites in Cu-BTC or coordinatively unsaturated Fe sites in MIL-88(Fe) [46,52]. Lueking and coworkers studied structural and dynamic behaviors of CO chemisorbed on copper paddlewheels of Cu-BTC [47]. Sauer and coworkers employed the quantum mechanical method to investigate the correlation between the type of the open metal site in M-MOF-74 and its binding strength with CO [48]. Dinca and coworkers recently designed a series of new mesoporous MOFs with extended bisbenzo-triazole ligands that contained coordinatively unsaturated metal sites, reporting that the open metal sites would be responsible for the high and reversible ammonia uptake [49]. Watanabe and Sholl employed the DFT method to investigate the properties associated with chemical interactions of various harmful gases, such as CO, NO, H_2S, and NH_3, with open metal sites in Cu-BTC [50]. Another primary approach introduced by researchers is to design polar functionality on surfaces of MOFs [53]. As stated early, an approach of N-rich functionalization has been primarily employed to design appropriate surface environments that would enable the strong dipole-quadrupole interaction between the surfaces and CO_2 for the selective CO_2 capture applications. On the other hand, the decoration of MOF surfaces for the selective capture of non-CO_2 harmful gases has been focused on introducing a broad range of functional groups with an aim of identifying appropriate functionality that would strongly bind targeted harmful gases [54–56]. For instance, Walton and coworkers studied the performance of various functionalized variations of a Zr-based MOF, UiO-