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Adsorption of volatile organic compounds over MIL-125-NH_2

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ABSTRACT

Volatile organic compounds (VOCs) cause environmental and health problems by forming photochemistry smog, and development of an effective adsorbent for their removal is important. In this work, adsorption of a series of selected VOCs over an amine-functionalized metal organic framework, MIL-125-NH_2, was investigated by measuring their adsorption isotherms at three different temperatures. Significant amounts of the VOCs were adsorbed, and their adsorption capacities increased with the increasing order of polarity (*p*-xylene < toluene < benzene < acetone < isopropanol). In addition, formaldehyde breakthrough capacities were measured and MIL-125-NH_2, exhibited a clearly superior performance to other MOFs, probably because of the synergistic effects provided by the amine groups that strongly interacting with the formaldehyde and the small micropores in MIL-125-NH_2.

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1. Introduction

Volatile organic compounds (VOCs) such as formaldehyde, BTXs (benzene, toluene, and xylenes), ketones, and alcohols, are among the most harmful organic species to the general public in indoor/outdoor environment, some of which are also known to be carcinogenic [1]. VOCs can also cause environmental and health risks by forming photochemistry smog [2], and mainly emitted from the chemical process industries, textile fabrics, building/construction materials, and indoor furniture paints [3].

Various methods including adsorption, condensation, ionization, and photocatalysis have been applied to remove VOCs from the contaminated air [4–6]. Among these, adsorption of VOCs over a porous material as adsorbent is a well-established and effective means for removal of VOCs in air. Zeolites [7], mesoporous silica or carbons [8,9], resins [10], and activated carbons together with other additives [11,12] have been utilized as adsorbents for VOCs. However, continued efforts are being made to develop a new porous material with large surface area and sufficient pore volume to achieve higher adsorption capacities for VOCs. In particular, while various adsorbents have been used to remove formaldehyde in liquid-phase [13,14], effective removal of it from indoor air remains challenging [15,16] due to its high polarity and reactivity compared with other VOCs, and difficulty for adsorption in the presence of humidity [17].

Metal–organic frameworks (MOFs) are a class of crystalline porous materials, composed of metal ions or clusters connected with organic linkers by coordination bonding in one-, two-, or three-dimensional networks [18]. It can be considered as a potential adsorbent for removal of VOCs because of their extremely large surface areas/pore volumes, tunable pore sizes, and various means available for post-synthesis organic-functionalization [19]. Their potential applications in gas adsorption [20], separation [21], and catalysis [22] have been well established.

Recently, some studies were carried out to investigate their adsorption behavior against VOCs [23–28]. Vellingiri et al. [23] studied the adsorption of toluene over six different MOFs (UiO-66, UiO-66-NH_2, MOF-199, ZIF-67, MIL-101(Fe), and MOF-5) under ambient conditions, and their adsorption capacity values (mg g^{-1}) were reported to be 166, 252, 159, 224, 98.3, and 32.9 mg g^{-1}, respectively. In particular, the adsorption performance of UiO-66-NH_2 was most reproducible when tested over a cycle of three runs (147 (1st) and 133 mg g^{-1} (3rd)). Yang et al. [24] studied the adsorption of VOCs covering both polar and nonpolar molecules on MIL-101, and explained the adsorption behavior by a pore filling mechanism and showed the size- and shape- selectivity towards the VOC molecules; acetone, benzene, toluene, ethylbenzene, and *p*-xylene can enter the MIL-101 pores, but *o*- and *m*-xylene cannot because of the long distance between the two methyl groups in them, which are longer than the pore diameters of MIL-101 (1.07 and 1.16 nm for *o*- and *m*-xylene, and 0.85–1.9 nm for MIL-101, respectively).

MIL-125 (Scheme 1), is prepared using titanium(IV) isopropoxide as the metal source and 1,4-benzene dicarboxylic acid (H_2BDC) as the linker. It is built up from cyclic octamers constructed from corner or edge sharing octahedral titanium units connected to oxygen atoms. These octamers are then connected to 12 other cyclic octamers through BDC linkers, leading to a porous three-dimensional

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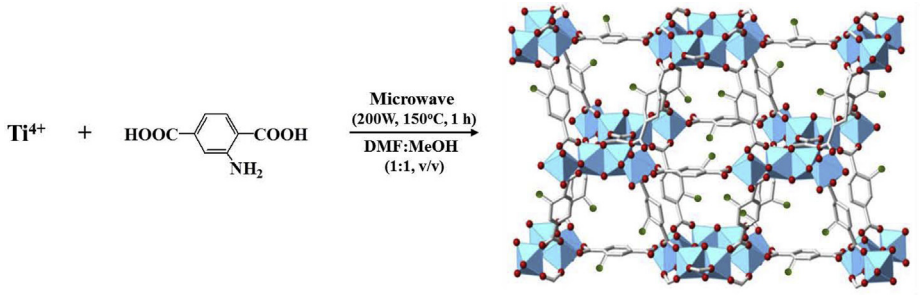

Scheme 1. Synthesis and crystal structure of MIL-125-NH_2.

quasi-cubic tetragonal structure having octahedral (~12.5 Å) and a tetrahedral (~6 Å) cages with triangular windows (5–7 Å) [22]. MIL-125-NH_2 is the amine-functionalized form of MIL-125, which is comprised of the basic unit of $Ti_8O_8(OH)_4$-(BDC-NH_2)$_6$, and can be prepared simply by replacing the organic ligand H_2BDC with 2-amino benzene dicarboxylic acid (H_2BDC-NH_2) in the substrate mixture. Excellent adsorption properties of MIL-125-NH_2 towards CO_2 [22] and selected chloroaromatic compounds [14] were reported earlier. Recently, Ahmed et al. [30] also reported that MIL-125-NH_2 exhibited efficient removal of nitrogen-containing compounds such as indole and quinoline, through interactions between the NH_2 groups in MIL-125-NH_2 and the compounds by forming hydrogen bonding. All these studies indicated that MIL125-NH_2 can be a potential candidate material for gas adsorption including organic vapors.

In this study, adsorption behavior of a series of VOCs over MIL-125-NH_2 was investigated. To be specific, the adsorption capacities for benzene, toluene, *p*-xylene, acetone, and isopropanol by MIL-125-NH_2 were measured by their adsorption isotherms at different temperature conditions, and the relationship between the specific surface area, pore size, functional groups of MOFs and their VOC adsorption capacities was examined. Furthermore, breakthrough capacity for formaldehyde by MIL-125-NH_2 was measured and compared with that by other different MOFs (MIL-125, UiO-66, UiO-66-NH_2, MIL-101, MIL-101-NH_2, and MIL-101-DETA), which established the contribution of the functional group and pore size in MOFs for effective adsorption of VOCs.

2. Experimental

2.1. Preparation of MIL-125-NH_2 and other MOFs

MIL-125-NH_2 was synthesized following the microwave heating procedure reported by Kim et al. [22]. To be specific, 0.6 mmol of titanium isopropoxide and 1.2 mmol of H_2BDC-NH_2 were dissolved in a 10 mL mixture solution of DMF and MeOH (1:1, v/v). The mixture was then introduced to a 35 mL glass tube sealed with a rubber septum and placed in a microwave oven (Discover S-class, CEM) and heated at 423 K for 1 h (200 W), and then cooled to room temperature. The yellow powder product was filtered and washed with DMF three times. Finally, the product was dried at 423 K for 12 h in vacuum.

Another six different MOFs were also synthesized and activated according to procedures reported in the literature: MIL-125, UiO-66, UiO-66-NH_2, MIL-101, MIL101-NH_2, and MIL-101-DETA (see Supplementary Information).

2.2. Characterization

The XRD patterns of the samples were obtained using Cu Kα radiation (λ = 1.54 Å) at a scanning rate of 0.5°/min. N_2 adsorption/desorption isotherms were measured using BELsorp-Max (BEL, Japan) at 77 K. Before the measurements, all the samples were activated; UiO-66, MIL-125, MIL-125-NH_2, and MIL-101 were degassed at 423 K for 12 h, whereas UiO-66-NH_2, MIL-101-NH_2, and MIL-101-DETA were activated at 373 K for 12 h. The specific surface areas of the samples were calculated using the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was estimated by the Horvath–Kawazoe (HK) method. The nitrogen contents of the MOF samples were measured by elemental analysis (EA, EA1112). Fourier transform infrared spectroscopy (FT-IR) was performed using a VERTEX 80 V (Bruker, Germany). Scanning electron microscopy (SEM) image was obtained using a Hitachi S-4300 microscope.

2.3. Adsorption experiments

2.3.1. Adsorption of benzene, toluene, p-xylene, acetone, and isopropanol by volumetric adsorption measurements

VOC adsorption isotherms under static conditions were obtained using a BELsorp-Max (BEL, Japan) at 293, 298, and 303 K over 80 mg of MIL-125-NH_2. This apparatus was modified with an additional organic vapor generation chamber with a heating system. Prior to adsorption, MIL-125-NH_2 was activated at 403 K for 12 h in vacuum. VOCs were generated by vaporizing the corresponding liquids in ultra-high vacuum at 313 K. The dissolved gas impurities were removed by repeating the process (5 times) of freezing VOC with liquid nitrogen and dissolving them in warm water bath. Adsorption equilibrium was assumed to be reached when the vapor pressure drop in the sample cell was less than 1 Pa within 5 min. The vapor pressure in the cell was measured using three 1, 10, and 1000 Torr transducers (accuracy of the transducers were ±0.15%, ±0.5% and ±0.25% of full scale, respectively). The adsorbed amount of VOCs on MIL-125-NH_2 at each pressure under adsorption equilibrium was calculated by the ideal gas law by the difference between the pressure at adsorption equilibrium and the initial vapor pressure in the sample cell.

The experimental adsorption data were then fitted to the Langmuir–Freundlich equation, and the corresponding heat of adsorption was calculated by applying the Clausius–Clapeyron equation as follows:

$$\left[\frac{\partial \ln P}{\partial \ln\left(\frac{1}{T}\right)}\right]_q = \frac{-\Delta H_{ads.}}{R}$$

where P is the pressure (kPa), T is the temperature (K), q is the amount adsorbed, R is the ideal gas constant (J mol^{-1} K^{-1}), and $\Delta H_{ads.}$ denotes the heat of adsorption (kJ mol^{-1}).

2.3.2. Adsorption of formaldehyde over a fixed-bed breakthrough unit

Adsorption performances of the MOFs (MIL-125, UiO-66, UiO-66-NH_2, MIL-125-NH_2, MIL-101, MIL-101-NH_2, and MIL-101-DETA) for formaldehyde were measured using a fixed-bed adsorption column. 20 mg of sample was packed into a stainless

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