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Selective dynamic separation of Xe and Kr in Co-MOF-74 through strong binding strength between Xe atom and unsaturated Co^{2+} site

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ABSTRACT

From pure experimental isotherms and ideal adsorbed solution theory (IAST), we confirmed a recent report that Co-MOF-74 provides the highest Xe uptake as well as the highest Xe/Kr selectivity among the three M-MOF-74 series (M = Co, Mg, and Zn). From breakthrough experiments, we then showed the first demonstration of the potential of Co-MOF-74 for Xe/Kr separations under mixture flow conditions. Remarkably, the experimental breakthrough curves for three consecutive cycles are essentially unchanged even if the column was regenerated under helium flows at room temperature between each cycle. Isosteric heat of adsorption (Q_{st}) for Xe, adsorbed Xe molecules per metal, and binding strengths and electronic density of states (DOS) analyses from first principles calculations all indicate that unsaturated Co^{2+} sites attract Xe more strongly than do unsaturated Mg^{2+} and Zn^{2+} sites. The DOS analyses show that the *d* orbital of the Co^{2+} is the main contributors for the strong interaction. These results suggest that Co-MOF-74 is a promising adsorbent for separations of Xe and Kr.

1. Introduction

The concentrations of the noble gases xenon and krypton in the atmosphere are 0.087 and 1.14 ppmv, respectively [1]. However, these gases are industrially valuable, with wide applications. Xenon is used in flash lamps, arc lamps, anaesthesia, neuroprotection, imaging, and NMR spectroscopy. Krypton is used in fluorescent lamps, photographic flashes, and magnetic resonance imaging [2]. During cryogenic distillation of air for separation of N_2 from O_2, a concentrated Xe/Kr mixture (20/80 M ratio) is obtained as a by-product. These mixtures were conventionally separated by further cryogenic distillation, which is highly energy- and capital-intensive [3–5]. Hence, adsorptive separation using porous materials has been considered as an energy- and cost-effective alternative. For the design of adsorptive separation processes such as pressure swing adsorption (PSA), a highly Xe-selective adsorbent with high capacity is essential [6]. Metal-organic frameworks (MOFs) are a new class of nanoporous material, with many attractive properties such as extremely high surface area, low density, and tailorable pore structures and functionalities [7–9]. Due to their interesting features, MOFs have been considered as potential adsorbents for many gas separation applications [10–16].

There have been several computational reports on separation of Xe and Kr using MOFs. From grand canonical Monte Carlo (GCMC) simulations, Greathouse et al. showed that a MOF, IRMOF-1, could separate Xe/Kr mixtures with modest selectivity (~3) [17]. Gurdal and Keskin did molecular simulations to examine adsorption, diffusion, and separation of Xe/Kr and Xe/Ar mixtures using ten representative MOFs, and showed that MOFs are promising candidates for separation of Xe from Kr and Ar [18]. Sholl et al. computationally screened over 3400 MOFs and identified 70 candidates for seven different noble gas separations [19]. From a high-throughput computational screening of 137,000 hypothetical MOFs, Snurr et al. concluded that MOFs with cylindrical pores just large enough to fit a single Xe atom would be ideal for separation of Xe and Kr [20].

In addition to these computational studies, experimental studies have been reported for a relatively small number of MOFs. Thallapally et al. showed that Ni/DOBDC has higher Xe/Kr selectivity than activated carbon or HKUST-1 [1,21]. They also found that a fluorinated MOF shows inverted adsorption selectivity toward Kr below 0 °C [22]. They have recently shown that sliver-loaded Ni/DOBDC improves Xe adsorption capacity [23]. Bae et al. showed that MOF-505 has high Xe/Kr selectivity due to small pores with strong

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adsorption sites [24]. Li et al. reported that $Co_3(HCOO)_6$ shows high Xe adsorption capacity and high Xe/Kr selectivity due to the unique size and shape of the channel structure [3]. Cooper et al. have recently reported that a porous organic cage molecule, though not a MOF, has potential for the separation of Kr, Xe and Rn from air at very dilute concentrations by a molecular sieving mechanism [25].

Previous studies have shown that a series of isostructural MOFs (M/DOBDC, M = Co, Mg, Zn, Ni, etc.) [26] have potential in separations of Xe and Kr from single-component adsorption isotherms [1,21,27]. M/DOBDC has the highest densities of unsaturated metal sites of any reported MOFs and is also referred to as M-MOF-74 [28], M_2(dhtp) [29] or CPO-27-M [30]. Perry et al. have recently investigated the adsorption of noble gases (Ar, Kr, Xe, and Rn) and N_2 in a diverse range of MOFs containing unsaturated metal sites by using volumetric gas porosimetry and GCMC simulations [27]. Among the large data sets from their study, experimental and simulated adsorption data of pure Xe and Kr on the M-MOF-74 series were included. Their experimental data consistently suggested that Co-MOF-74 exhibits the largest Xe and Kr uptakes, the highest Xe/Kr selectivity and the highest isosteric heat of adsorption (Q_{st}) for Xe. However, all of these experimental and simulation results are based on adsorptive measurements of pure Xe and Kr on MOF materials. To evaluate the potential industrial performance of Co-MOF-74 for Xe/Kr separations, we need to measure dynamic separation properties of a packed column under mixture flow conditions.

Perry et al. have also found that the M-MOF-74 series exhibits stronger interactions with noble gases than the NbO-type MOF series (NOTT-100, NOTT-101, NOTT-102, NOTT-103, and PCN-14) and HKUST-1, with higher heats of adsorption for all noble gases [27]. They attributed this to the increased accessibility of the open metal sites in the M-MOF-74 series consisting of the large hexagonal 1-D channel as well as the high density of open metal sites. However, the reason of the superior Xe/Kr selectivity of Co-MOF-74 among M-MOF-74 series is still needed to be understood.

In this work, we measured the experimental pure isotherms of Xe and Kr in the M-MOF-74 series (M = Co, Mg, and Zn) and calculated the Xe/Kr selectivities by using the ideal adsorbed solution theory (IAST) to confirm the report by Perry et al. We then obtained the experimental breakthrough curves under packed-bed mixture flow conditions to assess the potential of Co-MOF-74 for real adsorptive separation of Xe/Kr mixtures. We also investigated the reason why Co-MOF-74 exhibits the larger Xe/Kr selectivity than the other M-MOF-74 series. For this, we measured the Xe Q_{st} and the adsorbed Xe molecules per metal and calculated the binding strengths from density functional theory (DFT) calculations. To further determine the roles of the unsaturated cobalt sites in Co-MOF-74 for Xe adsorption, we calculated the electronic density of states (DOS) of the unsaturated metal sites and Xe atoms for the M-MOF-74 series.

2. Material and methods

2.1. Materials

Cobalt (II) nitrate hexahydrate, magnesium nitrate hexahydrate, zinc nitrate hexahydrate and 2,5-Dihydroxyterephthalic acid were purchased from Sigma-Aldrich Korea. All other reagents were of analytical grade and were used without further purification. Ultra-high purity N_2 (99.999%) was purchased from Air Korea, Co., Ltd. and used as received. High purity Xe (99.999%) and Kr (99.999%) were purchased from American Specialty Gases Inc. and used as received.

2.2. Preparation and characterization of M-MOF-74s

All MOFs were synthesized according to published procedures: Co-MOF-74 [26]; Mg-MOF-74 [31]; Zn-MOF-74 [31]. After synthesizing each MOF, the mother liquor was decanted and the remaining products replaced with methanol. For each MOF, the methanol solvent was decanted and replenished several times according to the corresponding published procedures.

Powder X-ray diffraction (PXRD) patterns were obtained with an Ultima IV diffractometer (Rigaku Co., Japan) using nickel-filtered Cu Kα radiation ($\lambda = 1.5418$ Å) from $5° < 2\theta < 30°$ in 0.02° steps at 1 s per step. Immediately before PXRD analyses, samples were collected as a thick suspension in methanol and spread on a fritted glass slide before being loaded into the diffractometer.

To obtain BET surface areas, N_2 adsorption and desorption measurements were performed on a TriStarII3020 system (Micromeritics Instruments, Norcross, GA 30093-2901, USA). After measuring the N_2 adsorption/desorption isotherms at 77 K at pressures up to 1 bar, specific surface areas were calculated using the Brunauer-Emmet-Teller (BET) model in the linear range using the following consistency criteria [32–34]: for Co-MOF-74: $0.0012 < P/P_0 < 0.0326$; for Mg-MOF-74: $0.0012 < P/P_0 < 0.0541$; for Zn-MOF-74: $0.0012 < P/P_0 < 0.0550$.

2.3. Adsorption measurements

The adsorption isotherms for Xe and Kr in the three MOFs were measured using an Autosorb-iQ system (Quantachrome Instruments, Boynton Beach, Florida, USA) with a specially designed water circulation system for maintaining constant temperature. For each sample, the isotherms were obtained at three different temperatures (283, 293 and 303 K) up to 1 bar. Samples were stored in a vacuum desiccator and quickly transferred to the sample holder of the adsorption equipment to prevent exposure to atmospheric moisture. Before each adsorption measurement including the BET measurement, approximately 100 mg of sample was degassed at 250 °C for 6 h under high vacuum ($<10^{-4}$ mbar).

2.4. Dynamic breakthrough experiments

The breakthrough experiments were carried out in a fixed bed experimental set up illustrated in Fig. 1. Three mass flow controllers (0–100 mL/min) (Bronkhorst, Germany) were used to regulate the gas flow rates. Two of them were used for pure Xe and Kr streams, which were mixed well with each other by flowing through a gas mixer. The other one was used for He stream for the in-situ regeneration of the column. The column was placed in a ventilated thermostatted oven for measurements at a constant temperature. The composition of the gas flow at the outlet of the column was measured online by a mass spectrometer (Pfeiffer Vacuum Prisma QME 200, Germany).

To avoid large pressure drops, the powder sample of Co-MOF-74 was pelletized using a carver press (Carver, Inc., USA). As-synthesized powders were put into a die with an inner diameter of 13 mm and pressed at 0.6 ton for about 1 min. The obtained solid disk was then crushed and sieved to obtain binderless Co-MOF-74 pellets with a size of 500–1000 μm. The obtained pellets were initially activated at 523 K for 5 h under vacuum. The activated pellets (82 mg) were then packed into a stainless steel column with a length of 5 cm and an internal diameter of 0.44 cm. The remainder of the column was filled with glass wools. The column was then degassed by a He flow of 30 mL/min at 353 K for 2 h to remove all the impurities adsorbed during the packing procedure. All the experiments were carried out at 303 K and 1 bar. Before each measurement, a He flow of 30 mL/min at 303 K was introduced into the column for at least 30 min. At t = 0, the He flow was switched to a flow of Xe/Kr mixture (Xe:Kr = 20:80, total flow rate = 30 mL/min).