Journal of Hazardous Materials 320 (2016) 513–520

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Adsorptive separation of xenon/krypton mixtures using a zirconium-based metal-organic framework with high hydrothermal and radioactive stabilities

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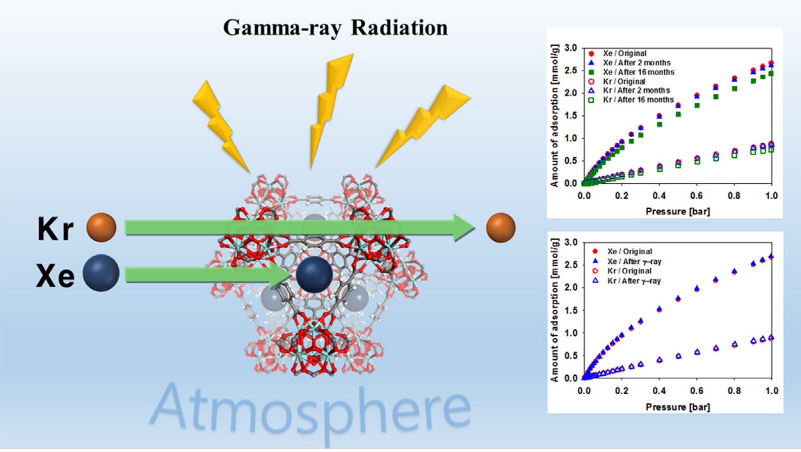
HIGHLIGHTS

- UiO-66(Zr) exhibits higher Xe/Kr selectivities than MIL-100(Fe) and MIL-101(Cr).
- UiO-66(Zr) can efficiently separate Xe/Kr mixture under dynamic flow conditions.
- The radioactive stability of UiO-66(Zr) is first demonstrated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 May 2016
Received in revised form 21 August 2016
Accepted 22 August 2016
Available online 24 August 2016

Keywords:
Xenon
Krypton
Rare gases
Metal-organic framework (MOF)
Separation
Adsorption

ABSTRACT

The separation of xenon/krypton mixtures is important for both environmental and industrial purposes. The potential of three hydrothermally stable MOFs (MIL-100(Fe), MIL-101(Cr), and UiO-66(Zr)) for use in Xe/Kr separation has been experimentally investigated. From the observed single-component Xe and Kr isotherms, isosteric heat of adsorption (Q_{st}^{o}), and IAST-predicted Xe/Kr selectivities, we observed that UiO-66(Zr) has the most potential as an adsorbent among the three candidate MOFs. We performed dynamic breakthrough experiments with an adsorption bed filled with UiO-66(Zr) to evaluate further the potential of UiO-66(Zr) for Xe/Kr separation under mixture flow conditions. Remarkably, the experimental breakthrough curves show that UiO-66(Zr) can efficiently separate the Xe/Kr mixture. Furthermore, UiO-66(Zr) maintains most of its Xe and Kr uptake capacity, as well as its crystallinity and internal surface area, even after exposure to gamma radiation (2 kGy) for 7 h and aging for 16 months under ambient conditions. This result indicates that UiO-66(Zr) can be considered to be a potential adsorbent for Xe/Kr mixtures under both ambient and radioactive conditions.

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http://dx.doi.org/10.1016/j.jhazmat.2016.08.057
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1. Introduction

The selective capture and storage of radioactive ^{85}Kr from effluent gas that contains Xe and Kr atoms from nuclear fuel reprocessing plants is important. Although ^{85}Kr is invisible and odorless, it can lead to climate change and potentially human diseases such as cancer or genetic diseases [1]. Currently, capital- and energy-intensive cryogenic distillation is used for the selective capture of ^{85}Kr from spent nuclear fuel [2]. The separation of xenon/krypton mixtures is also an important issue because both gases are valuable to industry because of their broad applications. Xenon and krypton are currently used in medical applications such as imaging and anesthesia, as well as in commercial lightning such as fluorescent lamps and photographic flashes [3]. Xe/Kr mixtures have conventionally been separated by cryogenic distillation to produce pure xenon and krypton [4,5]. However, this process consumes a significant amount of energy and has high capital costs [6]. Therefore, the adsorptive separation of Xe/Kr mixtures using porous materials has been considered as an energy- and cost-effective alternative [7].

Metal-organic frameworks (MOFs) are porous materials consisting of metal corners connected by organic ligands [8–10]. The modular synthetic strategy opens up the possibility to systematically vary chemical functionality and pore size in the search for an optimal material for a specific application [9,11,12]. Additionally, these materials have large surface areas, high porosity, and well-defined pore sizes. Due to these attractive features, MOFs have been considered as potential adsorbents for gas storage [13–16] or separations [17–23]. Until now, the studies on separations using MOFs have been primarily aimed at CO_2 separations [22–26] and hydrocarbon separations [27,28]. Studies on Xe/Kr separation using MOFs are relatively scarce [29].

Several computational [30–42] and experimental studies [2,4,38,40,41,43–49] have been performed on Xe/Kr separations in MOFs. From molecular simulations performed for 10 representative MOFs, Gurdal and Keskin [31] showed that MOFs have potential value in Xe/Kr and Xe/Ar separations. Sholl et al. [32] have identified 70 potential candidates for Xe/Kr, Ar/Kr, and Xe/Rn separations from a computational screening of over 3400 MOFs. Snurr et al. [34] suggested several MOF design criteria for Xe/Kr separation from a thermodynamic analysis of Xe/Kr selectivity in over 137,000 hypothetical MOFs. In a separate computational study, these researchers suggested that MOF-505 is the best material among the eight MOFs studied, considering both Xe adsorption capacity and Xe/Kr selectivity [33]. As a follow-up study, Bae et al. experimentally confirmed that MOF-505 has high selectivity for both Xe and Kr due to its small pores with strong adsorption sites [46]. From combined simulation and experimental studies, Greathouse, Allendorf and coworkers investigated noble gas adsorption in sixteen MOFs with different pore sizes and framework topologies [30] and studied the adsorption of several noble gases by ten MOFs with unsaturated metal sites [41]. Haranczyk et al. [37] have computationally screened a database of about 670,000 porous material structures including MOFs, all-silica zeolites, PPNs, ZIFs and COFs for candidate adsorbents for Xe/Kr separations. Thallapally and co-workers experimentally showed that Ni/DOBDC has a higher Xe/Kr selectivity than either activated carbon or HKUST-1 [44,45] and also showed that silver loading within Ni/DOBDC significantly enhances both Xe uptake capacity and Xe/Kr selectivity [2]. In another study, they experimentally demonstrated that two benchmark MOFs, Ni/DOBDC and FMOF-Cu, can capture and separate parts per million levels of Xe and Kr from air [49]. From a combined experimental and simulation study, they have recently studied the adsorption mechanism of noble gases in Ni/DOBDC [36]. Very recently, they demonstrated that SBMOF-1, identified as an outstanding Xe/Kr selective material from high-throughput computational screening over 125,000 MOFs, shows high Xe uptake, high Xe/Kr selectivity and good thermal and water stability [38].

Until now, experimental studies on Xe/Kr separations have only been performed for a limited number of MOFs. Additionally, although hydrothermal stability is an important issue for industrial applications [50], few studies have analyzed this attribute. In this work, we performed an experimental study in three MOFs (MIL-100(Fe) [51], MIL-101(Cr) [52], and UiO-66(Zr) [53]) to determine the potential of these materials for use in Xe/Kr separation. These three MOFs were selected due to their superior hydrothermal stabilities [53,54]. The single-component adsorption isotherms of Xe and Kr in the three adsorbents were measured at three different temperatures (283, 293 and 303 K). From these isotherm data, Xe/Kr selectivities were predicted by the ideal adsorbed solution theory (IAST). Packed-column breakthrough experiments were performed for the best-performing material, UiO-66(Zr), to evaluate its selective adsorption of Xe over Kr under dynamic mixture flow conditions. To confirm the hydrothermal stability of UiO-66(Zr), Xe and Kr isotherms were measured again after 2 and 16 months of storage, respectively, under ambient conditions. Furthermore, to evaluate the radioactive stability of UiO-66(Zr), Xe and Kr isotherms were measured after gamma radiation (2 kGy) for 7 h.

2. Experiments

All the MOFs were prepared according to published procedures: MIL-100(Fe) [51]; MIL-101(Cr) [52]; UiO-66(Zr) [53]. 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 Specialty Gases of America Inc. and used as received.

Powder X-ray diffraction (PXRD) patterns were obtained with a Ultima IV diffractometer (Rigaku Co., Japan) using nickel-filtered Cu Kα radiation ($\lambda = 1.5418$ Å) from $3^\circ < 2\theta < 30^\circ$ in 0.02° steps at 1 s per step. Immediately before the PXRD analyses, the samples were collected as a thick suspension in methanol and spread on a fritted glass slide before being loaded into the diffractometer.

To determine the BET surface areas, N_2 adsorption and desorption measurements were performed on an Autosorb-iQ system (Quantachrome Instruments, Boynton Beach, Florida, USA). After measuring the N_2 adsorption/desorption isotherms at 77 K at pressures up to 1 bar, the specific surface areas were calculated using the Brunauer-Emmet-Teller (BET) model in the linear range determined using the consistency criteria [55–57]: for MIL-100(Fe): $0.02733 < P/P_0 < 0.19999$; for MIL-101(Cr): $0.04712 < P/P_0 < 0.30129$; for UiO-66(Zr): $0.00703 < P/P_0 < 0.06638$. The adsorption isotherms for Xe and Kr in the three MOFs were also measured using an Autosorb-iQ system (Quantachrome Instruments, Boynton Beach, Florida, USA) with a specially designed water circulating system used to maintain a constant temperature. During the adsorption measurements, we stored the samples in a vacuum desiccator and quickly transferred the samples into the sample holder for the adsorption equipment to prevent exposure to moisture in the atmosphere. Before each adsorption measurement, approximately 100 mg of each sample was degassed at 250 °C (MIL-100(Fe), MIL-101(Cr)) or 120 °C (UiO-66(Zr)) under high vacuum ($<10^{-4}$ mbar).

The breakthrough experiments were carried out in a custom-built fixed bed experimental set up. 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 well-mixed with each other by flowing through a gas mixer. Another controller was used for the 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.