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Potential of Metal–Organic Frameworks for Separation of Xenon and Krypton

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Supporting Information

CONSPECTUS: The total world energy demand is predicted to rise significantly over the next few decades, primarily driven by the continuous growth of the developing world. With rapid depletion of nonrenewable traditional fossil fuels, which currently account for almost 86% of the worldwide energy output, the search for viable alternative energy resources is becoming more important from a national security and economic development standpoint. Nuclear energy, an emission-free, high-energy-density source produced by means of controlled nuclear fusion, is often considered as a clean, affordable alternative to fossil fuel. However, the successful installation of an efficient and economically viable industrial-scale process to properly sequester and mitigate the nuclear-fission-related, highly radioactive waste (e.g., used nuclear fuel (UNF)) is a prerequisite for any further development of nuclear energy in the near future. Reprocessing of UNF is often considered to be a logical way to minimize the volume of high-level radioactive waste, though the generation of volatile radionuclides during reprocessing raises a significant engineering challenge for its successful implementation. The volatile radionuclides include but are not limited to noble gases (predominately isotopes of Xe and Kr) and must be captured during the process to avoid being released into the environment. Currently, energy-intensive cryogenic distillation is the primary means to capture and separate radioactive noble gas isotopes during UNF reprocessing. A similar cryogenic process is implemented during commercial production of noble gases though removal from air. In light of their high commercial values, particularly in lighting and medical industries, and associated high production costs, alternate approaches for Xe/Kr capture and storage are of contemporary research interest. The proposed pathways for Xe/Kr removal and capture can essentially be divided in two categories: selective absorption by dissolution in solvents and physisorption on porous materials. Physisorption-based separation and adsorption on highly functional porous materials are promising alternatives to the energy-intensive cryogenic distillation process, where the adsorbents are characterized by high surface areas and thus high removal capacities and often can be chemically fine-tuned to enhance the adsorbate–adsorbent interactions for optimum selectivity. Several traditional porous adsorbents such as zeolites and activated carbon have been tested for noble gas capture but have shown low capacity, selectivity, and lack of modularity. Metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) are an emerging class of solid-state adsorbents that can be tailor-made for applications ranging from gas adsorption and separation to catalysis and sensing. Herein we give a concise summary of the background and development of Xe/Kr separation technologies with a focus on UNF reprocessing and the prospects of MOF-based adsorbents for that particular application.

1. INTRODUCTION

The worldwide demand for energy for the transportation and utility sectors continues to be a global interdisciplinary research challenge.1,2 The need is primarily driven by rapid population and industrial growth, which in turn leads to high energy consumption. Reports from the U.S. Department of Energy (DOE) indicate a ~28% increase in electrical demand by 2040.3 It is therefore imperative to devise a highly efficient, safe, and reliable energy solution that can satisfy these increasing demands in a way that does not further harm the land, water, and air.1,2

In the United States, electricity is predominately generated from fossil fuels, in addition to nuclear power and renewable energy. Nuclear energy continues to capture attention from both a scientific and political perspective, particularly in light of...
the Chernobyl disaster, the Three Mile Island incident, and the more recent 2011 tsunami and subsequent reactor meltdown in Fukushima, Japan. The tsunami impact on the Fukushima nuclear power plant and the surrounding areas prompted officials to revise existing nuclear safety protocols around the world. In spite of these localized incidents, nuclear power remains the leader in emission-free energy production, having an unparalleled energy density compared with other technologies as well as minimal land-use requirements.1−3 The production of radioactive used nuclear fuel (UNF) during energy generation in a nuclear power plant means that any future success depends on the development of alternative industrial-scale methods to properly sequester and mitigate the UNF. This non-biodegradable waste consists of a mixture of solid high-level waste, liquid low-level waste, and gaseous waste that can take thousands of years to decay, depending on which types of fission and activation products are generated.4 The majority of UNF is initially stored in deep, water-filled spent-fuel pools with steel-lined concrete walls that are several meters thick. The UNF can be reprocessed after cooling or transferred to leak-tight dry casks for storage until it can be transported to a permanent deep underground geologic repository.5,4

In an effort to extend the nuclear fuel supplies, minimize high volumes of radioactive waste, and recover precious isotopes, countries such as France, Japan, and Russia routinely reprocess UNF to recover plutonium and uranium from the irradiated fuel for advanced fuel cycles. However, volatile radionuclides generated during irradiation of the fuel are released into the plant off-gas streams during reprocessing and ultimately into the environment.4 These radionuclides include but are not limited to noble gases (isotopes of Xe and Kr), 3H, 14C, and 129I. The type of reprocessing method plays a key role in the types of gases that form these radionuclides. For example, in the case of aqueous reprocessing, the off-gas streams contain a mixture of noble gases (predominately 85Kr), tritiated water (3H2O or 3H2O), 14CO2, and iodine (H129I, 129I2, and organic iodides).4 Only 3H and 129I are captured in operating reprocessing facilities, while CO2 and Kr are released to the environment, resulting in the need to remove radioactive Kr and Xe (if present) when the UNF is reprocessed.

Currently, the United States does not reprocess and recycle UNF because of nuclear proliferation concerns, despite the fact that it has an estimated 70,000 t (and counting) of UNF in storage at nuclear facilities across the country.6 However, the government does recognize that the current storage technology is not a viable long-term solution, but strict licensing requirements in conjunction with high infrastructure/maintenance costs impede the use of existing reprocessing technologies.

2. XENON AND KRYPTON SEPARATION TECHNOLOGIES: WHERE DO WE STAND?

Nonradioactive xenon-based devices are ubiquitous in our daily lives, ranging from lighting and lasers to medical devices.7−9 However, while Xe and Kr are volatile noble gases that are available naturally in the atmosphere, they are exceptionally rare compared with other gases, with detectable concentrations of only 0.09 and 1.1 ppm, respectively. Commercially, these gases are removed from air by an energy-intensive cryogenic distillation method. The separation is accomplished on the basis of differences in the boiling point (e.g., −108.12 and −110 years before potentially being released into the atmosphere, when the majority of the Kr inventory (about 90%, depending on the age of the fuel) is nonradioactive.

The proposed alternatives for Xe/Kr removal can essentially be divided into two categories: selective absorption by dissolution in a solvent and physical adsorption on porous materials.5,12,13 In principle, the liquid absorption process would be carried out in a similar manner to cryogenic distillation, but the separation factor is governed by the solubility of the targeted gases in a particular solvent and varies as a function of temperature and pressure. For example, a team

![Figure 1. Thermodynamic properties of different noble gases.](image-url)
of researchers achieved $^{85}$Kr separation factors of up to 1000 and removal efficiencies of 99.9% by implementing an absorption into dichlorodifluoromethane (refrigerant-12, R-12) as a process solvent.\(^{13,14}\) This fluorocarbon absorption study was carried out on a pilot scale and offered several advantages, including low solvent and refrigeration costs along with reduced explosion hazards. Nevertheless, in order for this technology to be considered as a viable alternative, the operating pressures would need to be reduced and potential solvent losses from process leakage, volatilization, and radiolysis degradation would need to be addressed. Alternatively, CO\(_2\) solvent losses from process leakage, volatilization, and radiolysis operating pressures would need to be reduced and potential technology to be considered as a viable alternative, the study was carried out on a pilot scale and...t of researchers achieved $^{85}$Kr separation factors of up to 1000 and removal efficiencies of 99.9% by implementing an absorption into dichlorodifluoromethane (refrigerant-12, R-12) as a process solvent.\(^{13,14}\) This fluorocarbon absorption study was carried out on a pilot scale and offered several advantages, including low solvent and refrigeration costs along with reduced explosion hazards. Nevertheless, in order for this technology to be considered as a viable alternative, the operating pressures would need to be reduced and potential solvent losses from process leakage, volatilization, and radiolysis degradation would need to be addressed. Alternatively, CO\(_2\) solvent losses from process leakage, volatilization, and radiolysis operating pressures would need to be reduced and potential technology to be considered as a viable alternative, the study was carried out on a pilot scale and o...
packed with the activated material at 55 °C and 4 MPa. A significant improvement was observed for the Xe/Kr selectivity compared with activated carbons: the Xe concentration measured in the reactor outlet was reduced to 50 ppm because of the preferential adsorption of Xe in the MOF sorbent. We performed a dynamic breakthrough column measurement at 100 kPa and room temperature with pellets of commercially available HKUST-1. The single-component and binary breakthrough curves reveal that this material preferentially adsorbs Xe over Kr. However, the Xe capacity (3.18 mol/kg) was still lower than that of the benchmark activated carbon (3.72 mol/kg). Moreover, the selectivities measured for three gas compositions (i.e., Xe/Kr = 20:80, 50:50, 80:20) were consistently lower than those for activated carbon (e.g., ~2.6 at 100 kPa). Interestingly, in accordance with nuclear fuel reprocessing applications, HKUST-1 was found to selectively adsorb low (ppm) concentrations of Xe over Kr. However, the Xe capacity (3.18 mol/kg) was still lower than that of the benchmark activated carbon (3.72 mol/kg). Moreover, the selectivities measured for three gas compositions (i.e., Xe/Kr = 20:80, 50:50, 80:20) were consistently lower than those for activated carbon (e.g., ~2.6 at 100 kPa). Interestingly, in accordance with nuclear fuel reprocessing applications, HKUST-1 was found to selectively adsorb low (ppm) concentrations of Xe over Kr from air (e.g., N₂, 78%; O₂, 21%; Ar, 0.9%; CO₂, 0.03%, etc.) with values comparable to those for activated carbon. To pinpoint the preferred adsorption sites of Xe in HKUST-1 and thereby understand the mechanism of Xe/Kr selectivity, studies were conducted using several analytical techniques including ¹²⁹Xe NMR spectroscopy, grand-canonical Monte Carlo (GCMC) simulations, and synchrotron neutron and X-ray diffraction. These results, most notably those by Hulvey and co-workers, confirmed the location of the favorable Xe adsorption site as being the small pockets and the surrounding windows leading to the cavity. This is in contrast to what was observed for other gases (e.g., H₂, CO₂), where the adsorbate primary interaction site is the accessible unsaturated Cu(II) center.

3.3. FMOFCu

FMOFCu is a twofold-interpenetrated, partially fluorinated Cu-based MOF in which copper paddlewheel SBUs are connected by ditopic V-shaped 4,4'-hexafluoroisopropylidenebis(benzoate) (hfipbb) linkers to form the overall 3-periodic framework. This particular MOF was specifically selected by us for Xe/Kr adsorption studies because of its potential to exhibit a “molecular sieving” effect. The pore structure contains tubular cavities (ca. 0.51 nm × 0.51 nm) with bottleneck windows having estimated dimensions of 0.35 nm × 0.35 nm. Accordingly, under the appropriate conditions it was possible for Kr to be selectively adsorbed over Xe, as their kinetic diameters are 0.36 and 0.39 nm, respectively. Most porous adsorbents (e.g., zeolites) preferentially adsorb Xe over Kr, a process primarily driven by the higher polarizability of Xe atoms. Indeed, pure-component gas adsorption isotherms confirmed that FMOFCu is selective toward Kr (termed

![Figure 2. (a) Crystal structure of FMOFCu. The 1D open channels are connected through the bottleneck windows. Color code: Cu, green; C, gray; O, red. All hydrogen atoms and guest molecules have been omitted for clarity. (b, c) Variable-temperature pure-component (b) Kr and (c) Xe adsorption isotherms for FMOFCu collected up to pressures of 1 bar at six temperatures ranging from −70 to 40 °C. Reproduced from ref 22. Copyright 2012 American Chemical Society.](dx.doi.org/10.1021/ar5003126)
The behavior was temperature-dependent and observed only below 0 °C (Figure 2). The selectivity was reversed above 0 °C, where the Xe and Kr adsorption capacities were comparable across the entire pressure range. The lowest Xe capacity was observed at ~70 °C, probably because of the contraction of the bottleneck windows. The windows appeared comparable to that of activated carbon (Figure 3). However, it showed that the adsorption performance and selectivity was reverse selectivity behavior was predicted by computational studies, though the example of FMOFCu remains the only experimental report to date.

3.4. M-DOBDC (M-MOF-74)

M-DOBDC (M = Mg, Mn, Fe, Co, Ni, Zn; DOBDC = 2,5-dihydroxyterephthalate; MOF-74-M) is a class of isostructural microporous MOFs with regular, hexagonal unidimensional pores decorated with open metal sites at the pore surface. The presence of abundant, accessible open metal sites and the significant porosity (~1000–1500 m²/g) leads to excellent adsorption properties for various adsorbates. We carried out adsorption experiments on Ni-DOBDC and found that it has a Xe adsorption capacity of 55 wt % at 100 kPa and 298 K, twice that of activated carbon. The Xe adsorption capacity of 55 wt % at 100 kPa and 298 K, while the adsorption isotherm for Kr was found to be linear. As expected from the nature of isotherms, a greater Q ads for Xe (22 kJ/mol) than for Kr (22 kJ/mol) was calculated for Co3(HCOO)6 and similar Q ads trends were also observed for the other isostructural metal analogues (Figure 5). The follow-up breakthrough experiments backed up the Xe selectivity (~6) for the M3(HCOO)6 series. Simulations showed that each Xe atom optimally fits within a segment (i.e., a zig or a zag) and thus can interact more effectively with the π cloud of the formate groups on the pore surface.

3.5. M3(HCOO)6

Among a diverse range of metal formates, M3(HCOO)6 (M = Mg, Ni, Co, Zn, Mn) is particularly noteworthy because of its simplistic diamondoid topology and the existence of a zigzag channel with an effective pore size of 0.5 to 0.6 nm. The adsorption of Xe in nanoporous Co3(HCOO)6 shows a type I adsorption isotherm (26 wt % at 25 °C and 100 kPa), while the adsorption isotherm for Kr was found to be linear. As expected from the nature of isotherms, a greater Q ads for Xe (29 kJ/mol) than for Kr (22 kJ/mol) was calculated for Co3(HCOO)6 and similar Q ads trends were also observed for the other isostructural metal analogues (Figure 5). The follow-up breakthrough experiments backed up the Xe selectivity (~6) for the M3(HCOO)6 series. Simulations showed that each Xe atom optimally fits within a segment (i.e., a zig or a zag) and thus can interact more effectively with the π cloud of the formate groups on the pore surface.

3.6. MOF-505

MOF-505 is a 3-periodic MOF composed of copper paddlewheel SBUs connected by the organic linker bipyren-3,3′,5,5′-tetracarboxylate (bptc), forming different pore diameters (0.48, 0.71, and 0.95 nm). Bae and co-workers chose MOF-505 on the basis of published simulation studies showing a high Xe/Kr selectivity over the typical operating pressure range.
range (0.1 to 1 MPa).\textsuperscript{23,29} The breakthrough experiment with a 20:80 mixture of Xe and Kr indicated a much higher retention time for Xe compared with Kr, and the selectivity was calculated to be 9\textsuperscript{−10}, in line with the results of the simulations. The higher Xe selectivity is attributed to the pore confinement effect and the presence of “polarizable” open metal sites of the paddle wheel SBUs at the pore surface.

### 3.7. Comparison of the Separation Performance of Various MOFs

The separation performance of MOFs in industrial fixed-bed adsorbers is governed by a combination of three factors: (a) adsorption selectivity, (b) uptake capacity, and (c) intracrystalline diffusivities of guest molecules.\textsuperscript{33} The selection of MOFs solely on the basis of adsorption selectivity, as is commonly done in published studies, often leads to misleading conclusions.\textsuperscript{29} To illustrate this, we consider the separation of 20:80 Xe/Kr mixtures by each of six MOFs: Ni-DOBDC, Ag@Ni-DOBDC, HKUST-1, IRMOF-1, FMOFCu, and Co\textsubscript{3}(HCOO)\textsubscript{6}. The hierarchy of Xe/Kr adsorption selectivities is Co\textsubscript{3}(HCOO)\textsubscript{6} > Ag@Ni-DOBDC > Ni-DOBDC > HKUST-1 > IRMOF-1 > FMOFCu. The Xe uptake capacities follow a different hierarchy: Ag@Ni-DOBDC > Ni-DOBDC > Co\textsubscript{3}(HCOO)\textsubscript{6} > HKUST-1 > IRMOF-1 > FMOFCu (Figure 6). Transient breakthrough simulations are potent tools for comparing the separation performance of MOFs because they take proper account of selectivity, uptake capacity, and diffusion limitations. The breakthrough characteristics of 20:80 Xe/Kr mixtures in fixed beds packed with each of the six MOFs are shown in Figure 7 (see the Supporting Information for simulation details). Both IRMOF-1 and FMOFCu are incapable of producing Kr of the desired purity. The longest breakthrough time is obtained with Ag@Ni-DOBDC; consequently, this MOF is the best to produce Kr with the desired purity level (see the Supporting Information for a video animation). The hierarchy of Kr selectivities is Ag@Ni-DOBDC > Ni-DOBDC > Co\textsubscript{3}(HCOO)\textsubscript{6} > HKUST-1. It should be noted that because of the lower Xe uptake capacity and diffusion limitations, Co\textsubscript{3}(HCOO)\textsubscript{6}, which has the highest Xe/Kr selectivity, performs significantly poorer than Ag@Ni-DOBDC.

### 3.8. Computational Studies

The number of potential MOFs for Xe/Kr separation is enormous, with many new novel structures produced weekly. However, because of time constraints and lack of available resources, it is not feasible for experimentalists to systematically screen all MOFs for their gas adsorption behavior. In an effort to alleviate this dilemma, the use of computational methods has gained momentum and provided valuable insight toward the development of structure–property trends that allow the
adsorption properties for a given material (e.g., capacity, selectivity, diffusion, preferred adsorption sites, etc.) to be simulated for both existing and hypothetical MOFs.\textsuperscript{9,30,34} Sikora and co-workers used high-throughput computational methods to generate 137,000 hypothetical MOFs possessing assorted coordination modes, chemical compositions, pore sizes, and morphologies.\textsuperscript{30} The Xe/Kr adsorption data generated from GCMC simulations confirmed that the pore size and shape play a fundamental role in governing the adsorbate–MOF interactions. Enhanced selectivity was observed for structures having tubelike uniform pores with diameters large enough to accommodate at most one Xe atom. However, a promising candidate must also exhibit high uptake capacities, and therefore, a fine balance exists between optimal pore size and surface area. This was exemplified by Ryan and co-workers, who performed GCMC simulations on a series of prominent MOFs with diverse chemical and structural characteristics.\textsuperscript{29} Not surprisingly, they found that MOFs with higher surface area adsorb larger amounts of Xe and Kr and thus exhibit lower selectivity. Accordingly, among all of the MOFs tested, Pd-MOF is the most selective sorbent for Xe/Kr, but its low adsorption capacity leaves plenty of room for improvement. Given the diverse nature and internal complexity of these materials, employing the computer simulation results is often not straightforward and in many cases involves approximations that have the potential to significantly affect the outcome. In general, reported differences between simulated and experimental results commonly arise from sample preparation and activation procedures and impurities, pore blockage, particle size, and insufficient amount of sample for sorption analysis.\textsuperscript{34} From a modeling perspective, differences could be attributed to the applied force field parameters (e.g., rigid vs flexible), taking into account or neglecting polarization, charges, etc. In order to produce high-quality data, it is therefore imperative to perform Brunauer–Emmett–Teller screening measurements to ensure that the appropriate solvent system and activation temperature are employed in order to fully exploit the available porosity of the MOF.

4. FUTURE SCOPE AND OUTLOOK

Porous MOFs are advantageous over other adsorbents because they can be tailored for specific applications. However, as of the date of this article, no large-scale commercial use of MOF-based adsorbents has been reported. Traditionally, MOFs have been envisioned for applications related to carbon capture and sequestration, \( \text{H}_2 \) storage, and hydrocarbon separation. Since the scale of these applications is enormous, material cost is a major consideration for any practical application. Unlike industrial adsorbents such as zeolites, large-scale production of MOFs is rare. However, with advances in synthetic methodology and appropriate monetary investment in large-scale linker synthesis, MOF prices comparable to those of synthetic zeolites may be possible in the near future. The separation of Xe and Kr during UNF reprocessing is comparatively small-scale, and the cost of the adsorbent material may not have a major impact on the overall cost of a process based on MOFs (though the quality of separation does\textsuperscript{4}). The separation of Xe and Kr in MOF-based solid-state adsorbents occurs as a function of adsorbate size and polarizability. On the basis of our own experimental work on Xe/Kr separation using MOF-based adsorbents, it is clear that an ideal material should have one or more of the following properties: (a) the presence of a high concentration of polar or accessible unsaturated metal centers on the pore surface (e.g., Ni-DODBC); (b) narrow uniform pores or pockets with diameters that are slightly larger than the kinetic diameter of the adsorbate (e.g., Co\(_3\)(HCOO)\(_6\), CC3, and FMOFCu); (c) the introduction of polarized nanoparticles within the MOF (e.g., Ag@Ni-DODBC); (d) temperature-dependent separation of the gas mixture (e.g., FMOFCu). Since it is highly unlikely that one single adsorbent will have all of the desired properties, an optimal MOF-based solid-state adsorbent system for Xe/Kr separation might eventually be obtained by a combination approach in which multiple MOF adsorbents are used to separate and capture Xe and Kr from the flue gas stream. We recently reported such a combination approach where a two-MOF system was used to obtain much higher separation performance. As mentioned previously, MOFs are more selective toward Xe over Kr because of the polarizability difference. However, the presence of excess Xe in the stream means that Xe competes for the same adsorption sites in the MOF as Kr. The use of a material with high Xe adsorption capacity (e.g., Ni-DODBC) first leads to reduction of the concentration of Xe in the flue gas stream. The gas stream can then be flowed through a second material with high Kr selectivity (e.g., FMOFCu) to capture and sequester Kr from the flue gas. Since Xe is no longer present to compete for sorption sites in the adsorbent in the second material, the capacity and selectivity for Kr increases significantly.\textsuperscript{12,32} Apart from the engineering challenges, the use of advanced computer programs to estimate and analyze the selectivities and capacities for MOF adsorbents is a major breakthrough. Computer simulations give direction for experimentalists to narrow their search for potential MOF structures and compositions from the enormous database or to design a new MOF by novel synthetic strategies. The application of computer simulations in predicting tailor-made MOF morphologies is likely to advance in the future with improvements in software and computing power. Finally, the adsorptive separation of Xe and Kr on porous MOFs is a relatively new research area, and relatively few materials have been evaluated to date. The deliberate tuning of the crystal structure and composition using crystal engineering principles, guided by the results of computational studies, to form MOFs that are tailored specifically for the separation of Xe and Kr is likely to yield further fundamental and applied results in the near future.

ASSOCIATED CONTENT

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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The authors declare no competing financial interest.

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REFERENCES
(28) Bohlmann, W.; Poppl, A.; Sabo, M.; Kaskel, S. Characterization of the metal–organic framework compound Cu(benzene-1,3,5-


