Selective, High-Temperature O₂ Adsorption in Chemically Reduced, Redox-Active Iron-Pyrazolate Metal–Organic Frameworks

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ABSTRACT: Developing O₂-selective adsorbents that can produce high-purity oxygen from air remains a significant challenge. Here, we show that chemically reduced metal–organic framework materials of the type AₙFe₂(bdp)ₓ (A = Na⁺, K⁺, bdp⁻ = 1,4-benzenedipyrazolate; 0 < x ≤ 2), which feature coordinatively saturated iron centers, are capable of strong and selective adsorption of O₂ over N₂ at ambient (25 °C) or even elevated (200 °C) temperature. A combination of gas adsorption analysis, single-crystal X-ray diffraction, magnetic susceptibility measurements, and a range of spectroscopic methods, including ²³Na solid-state NMR, Mössbauer, and X-ray photoelectron spectroscopies, are employed as probes of O₂ uptake. Significantly, the results support a selective adsorption mechanism involving outer-sphere electron transfer from the framework to form superoxide species, which are subsequently stabilized by intercalated alkali metal cations that reside in the one-dimensional triangular pores of the structure. We further demonstrate O₂ uptake behavior similar to that of AₙFe₂(bdp)₀ in an expanded-pore framework analogue and thereby gain additional insight into the O₂ adsorption mechanism. The chemical reduction of a robust metal–organic framework to render it capable of binding O₂ through such an outer-sphere electron transfer mechanism represents a promising and underexplored strategy for the design of next-generation O₂ adsorbents.

INTRODUCTION

The isolation of high-purity oxygen from air is vital for pre-combustion (i.e., carbonaceous fuel gasification) and post-combustion (i.e., oxy-fuel combustion) carbon capture technologies, as well as for the steel, medical, chemical, food, glass, and waste-treatment industries. Currently, purification methods such as cryogenic distillation are carried out on a large scale in industry, although these separations require enormous energy inputs. On smaller scales, membranes can increase O₂ concentrations relative to air, but they are typically capable of only ~50% enrichment. Porous adsorbents stand as attractive alternatives for O₂ purification, given that they can operate with high energy efficiencies and therefore at lower cost than low-temperature methods. However, the cation-exchanged zeolites currently employed in adsorbent-based air separation are generally N₂-selective and must be regenerated frequently, due to the larger nitrogen fraction in air (78%) as compared to oxygen (21%). Furthermore, the purity of oxygen derived from these zeolite adsorbents is also typically limited to ≤95%. The development of an O₂-selective adsorbent, especially one capable of separating oxygen at ambient or elevated temperature, could both enhance efficiency for this important industrial separation and facilitate technologies that mediate CO₂ release into the atmosphere. Indeed, in pre-combustion carbon capture—where carbonaceous fuel is gasified using high-purity O₂ converted to syngas, and combusted to power a turbine—significant efficiency gains are achieved by feeding air to the separation unit directly from the turbine compressor. In this integrated gasification combined cycle, air from the turbine compressor can exceed 300 °C due to compressive heating, and this heat must be rejected before entering the separation unit. Consequently, substantial energy savings could be achieved using an air separation unit capable of operating well above ambient temperature.

The design of O₂-selective adsorbents is particularly challenging given the similar physical properties of O₂ and N₂, such as kinetic diameter, polarizability, and quadrupole moment. Nitrogen is slightly greater in both polarizability and quadrupole moment, factors that are exploited by N₂-selective zeolites. Redox activity, however, is perhaps the most powerful characteristic of O₂ that distinguishes it from N₂. Indeed, biological systems leverage strategies based on redox activity to...
reversibly bind dioxygen, and similar behavior has been engineered in synthetic complexes and porous metal–organic frameworks through the use of coordinatively unsaturated, redox-active metal centers that provide open binding sites for O2. Depending on the electronic properties of the metal centers and the coordination environments in these systems, O2 can be reduced to either a superoxo (O2−) or a peroxo (O22−) species and can exhibit a variety of binding modes.

Given their high tunability, crystallinity, and chemical versatility, metal–organic frameworks can provide appealing platforms for the design of O2-selective adsorbents. Indeed, frameworks such as Cr3(btc)2 (btc3− = 1,3,5-benzenetricarboxylate), Cr-BTT (BTT3− = 1,3,5-benzenetriazatrole), Fe2(dobdc) (dobdc4− = 2,5-dioxido-1,4-benzenedicarboxylate), Co-BTTri (H3BTTri = 1,3,5-tri(1H-1,2,3-triazol-5-yl)benzene), Fe-BTTri, PCN-224MnII, and Co2(OH)2(bbta) (H2bbta = 1H,5H-benzo(1,2-d:4,5-d’)-bistriazole) have shown high selectivities and capacities for O2. However, oxygen binding in many of these materials is either irreversible or very weak at ambient temperature, and the frameworks tend to suffer from poor thermal stability, capacity loss during cycling, or framework degradation under humid conditions. Given that only a small fraction of all reported metal–organic frameworks feature open metal sites and the tunable design of such frameworks remains a considerable challenge, it is crucial to explore alternate design strategies.

To improve the energy efficiency of air separation processes, an ideal adsorbent would be highly selective for O2 and stable at ambient and even elevated temperature. In seeking underexplored O2 adsorption routes, we considered the possibility of outer-sphere electron transfer from coordinatively unsaturated, redox-active metal centers to provide open binding sites for O2. Depending on the electronic properties of the metal centers and the coordination environments in these systems, O2 can be reduced to either a superoxo (O2−) or a peroxo (O22−) species and can exhibit a variety of binding modes.

Figure 1. X-ray crystal structures of Fe2(bdp)3 (left), Na0.5Fe2(bdp)3 (middle), and room-temperature O2-dosed Na1.2Fe2(bdp)3 (right). Orange, blue, gray, red, and purple spheres represent Fe, N, C, O, and Na atoms, respectively. Disordered atoms and H atoms are omitted for clarity.

**RESULTS AND DISCUSSION**

**Synthesis and Characterization.** The synthesis of Fe2(bdp)3 was performed following the previously reported procedure to afford a black microcrystalline solid. The structure of this material consists of one-dimensional μ2-pyrazolate-bridged chains of octahedrally coordinated iron(III) nodes, connected in three dimensions by bdp5− linkers to yield a rigid framework with triangular channels (Figure 1). Importantly, the strong metal–pyrazolate bonds and structural rigidity of the framework should serve to prevent coordinative reorganization or material degradation upon O2 adsorption.

Subsequent reduction of Fe2(bdp)3 with sodium or potassium naphthalenide in tetrahydrofuran yielded AFe2(bdp)3 (A = Na+, K+; 0 ≤ x ≤ 2) in a topotactic manner, as previously described. Langmuir surface areas of 750–790 m2/g were reliably obtained for the half-reduced framework materials AFe2(bdp)3 following activation at 180 °C, whereas the fully reduced compound A2Fe2(bdp)3 was found to be essentially nonporous to N2. We therefore narrowed our initial focus to the half-reduced form of this framework due to its greater accessible porosity. Additionally, on the basis of its electrochemical behavior, AFe2(bdp)3 is less reducing than A2Fe2(bdp)3, which should favor the formation of superoxo rather than peroxo species. We note that, because superoxide is a one-electron reduction product of O2, a material that favors an alkali-stabilized superoxo species in its pores has twice the theoretical capacity of one that generates a peroxo species. Superoxo binding is also more likely to be reversible than peroxo binding, and indeed peroxo binding is often irreversible, as has been observed at elevated temperature for Fe2(dobdc). We further focused our initial studies on the potassiated congener, due to the relative stability of potassium superoxide as compared to sodium superoxide.
O₂ Adsorption in Reduced Fe₂(bdp)₃. We initially probed the interaction of reduced Fe₂(bdp)₃ with dioxygen by measuring the O₂ adsorption isotherm of K₁₀.₀₉Fe₂(bdp)₃ at 298 K (Figure 2). Powder X-ray diffraction data collected at this temperature confirmed no loss of crystallinity or change in symmetry upon O₂ dosing (Figure S1). At low pressures, the material exhibits an extraordinarily steep uptake of O₂ (Figure 2) and achieves a loading of 0.44 mmol/g at just 1 mbar O₂. The O₂ uptake thereafter rises only gradually with increasing pressure, to result in a loading of 0.51 mmol/g at 0.21 bar—close to the partial pressure of O₂ in air—and a maximum loading of 0.68 mmol/g at 1 bar. The steep O₂ uptake is suggestive of strong initial adsorption, whereas in contrast, K₁₀.₀₉Fe₂(bdp)₃ exhibits little N₂ adsorption under these conditions, consistent with only weak physisorptive guest-framework interactions. The O₂ and N₂ adsorption isotherms were modeled using multisite and single-site Langmuir-Freundlich equations, respectively (Figure S2; see details in the Supporting Information), and the strong interaction of the framework with O₂ is exemplified by far higher Langmuir parameter values (Table S1). Given the stark differences in the O₂ and N₂ adsorption profiles, we would further expect near-perfect selectivity for O₂ over N₂ under the measured conditions. Many empirical and theoretical frameworks for describing adsorption, such as Ideal Adsorbed Solution Theory, poorly predict adsorption equilibria for mixtures containing adsorbates with substantially differing adsorption interactions (e.g., chemisorption as compared to physisorption) and for adsorbents with heterogeneous surfaces (e.g., cation-exchanged zeolites). Nevertheless, a full discussion of multiple methods we used to quantify the selectivity and strength of O₂ binding is available in the Supporting Information. These calculations show that O₂ can be efficiently separated from N₂ even at very low O₂ partial pressure. Furthermore, given the proper conditions for regeneration of this material after air separation, it is likely that O₂ with a purity greater than 99.9% could be generated.

The framework uptake of 0.51 mmol/g (0.40 molecules of O₂ per formula unit, Figure S4) at 0.21 bar of O₂ corresponds to approximately 40% of the theoretical capacity (1.40 mmol/g) given a stoichiometry of K₁₀.₀₉Fe₂(bdp)₃ and assuming one-electron reduction of O₂ to form superxo species. This result implies that either a more reduced dioxygen species is being formed or there is a kinetic barrier to complete O₂ loading. Indeed, if the O₂ uptake at ambient temperature is kinetically limited, a substantial increase in available thermal energy could surmount the activation barrier and enable access to the full capacity of the material, if one assumes no change in the mechanism of adsorption. Examples of kinetic limitations could include hindered diffusion through the narrow triangular framework channels due to occlusion by reduced O₂ species, an activation barrier toward rearrangement of alkali cations upon introduction of O₂, sluggish movement of reduced O₂ species to preferred binding sites, or even a barrier to electron transfer.

Seeking to explain this partial loading, as well as to test the chemical stability of the material, we further measured O₂ adsorption at 473 K (200 °C). Significantly, K₁₀.₀₉Fe₂(bdp)₃ retains its strong affinity for O₂ at this temperature and displays an enhanced adsorption capacity (Figure 2), to achieve a loading of 0.98 mmol/g at 10 mbar. Subsequent dosing yielded loadings of 1.11 and 1.32 mmol/g at close to 0.21 and 1.0 bar, respectively. The uptake at 0.21 bar of O₂ corresponds to 0.86 molecules of O₂ per formula unit (Figure S4) or ~80% of the theoretical capacity, which critically rules out the formation of a peroxo species, at least at 473 K. On the basis of these data, we again expect the O₂/N₂ selectivity of K₁₀.₀₉Fe₂(bdp)₃ at 473 K to be extraordinarily high. The apparent selectivity of this material for O₂ at ambient temperature and the substantial increase in capacity at such a high temperature ultimately indicate its great promise for O₂ separations.

Desorption isotherms collected for K₁₀.₀₉Fe₂(bdp)₃ at 298 K show only the release of weakly bound O₂ (Figure S5), while the majority remains strongly adsorbed. A small amount of hysteresis is observed, likely due to strong but highly kinetically limited binding of O₂ during the shallow uptake region of the adsorption isotherm that is not removed upon desorption. However, upon heating to 453 K (180 °C) under vacuum after an adsorption and desorption isotherm cycle, the material can be partially regenerated. Over at least five adsorption/desorption cycles between 0 and 0.21 bar at 298 K followed by activation, the quantity of O₂ adsorbed during each adsorption isotherm appears to reach an asymptotic value of ~0.2 mmol/g (Figure S6). We note that the regeneration conditions were not optimized, and indeed we found that heating to 478 K (205 °C) under vacuum resulted in greater capacity recovery. Thus, higher regeneration temperatures and longer regeneration times may allow for more of the capacity of the material to be recovered. In fact, desorption at 473 K appears to be more reversible in the low-pressure region than at 298 K (Figure S7), and impressively the material can be cycled at least 10 times at these elevated temperatures, albeit with diminished capacities (Figure S8).

We also measured 298 and 473 K O₂ adsorption isotherms for Na₁₄.₀₉Fe₂(bdp)₃ (Figure S9), which displayed behavior almost identical to that of the potassiated version. Thus, the stability of the reduced O₂ species within the framework pores appears not to be strongly dependent on the alkali metal cation, although complex cations could show different behavior.

The foregoing results imply that the adsorption of O₂ in AₙFe₂(bdp)₃ is either under kinetic control to some degree or that the mechanism of O₂ adsorption is altered at elevated temperatures.
temperature. We therefore sought a deeper understanding of (i) the lower \( O_2 \) uptake at ambient temperature—for example, whether \( O_2 \) diffusion is limited as described above—and (ii) the nature of the adsorbed \( O_2 \) species.

**Single-Crystal X-ray Structure Determinations.** Single-crystal X-ray diffraction was employed to determine the nature of the adsorbed \( O_2 \) species in \( A_i \text{Fe}_2 \text{(bdp)}_3 \) and the adsorption mechanism. Dark, acicular, X-ray quality single crystals of \( \text{Fe}_2 \text{(bdp)}_3 \) were synthesized using a modification of the original synthetic procedure (see the Supporting Information).\(^{32}\) Following chemical reduction, activation, and room-temperature \( O_2 \) dosing of the crystals (details available in the Supporting Information), we obtained structures of both Na- and K-reduced \( \text{Fe}_2 \text{(bdp)}_3 \) (Figures 1 and 3). Virtually the same

![Figure 3. Expanded sideview along one pore of \( \text{K}_{1.06} \text{Fe}_2 \text{(bdp)}_3 \) dosed with 1 bar \( O_2 \) at 298 K. Orange, gray, blue, red, and green spheres represent \( \text{Fe} \), \( C \), \( N \), \( O \), and \( K \) atoms, respectively. Both crystallographically distinct K sites are shown. Disordered atoms created by symmetry and hydrogen atoms are omitted for clarity.](image-url)

Fe–N bond lengths and ligand metrical parameters were found for reduced \( \text{Fe}_2 \text{(bdp)}_3 \) and its \( O_2 \)-dosed form; however, the pores of the latter structure are clearly occupied by \( O_2 \) species stabilized by intercalated cations. We note that the absence of observable \( O_2 \) species near the iron centers also helps refute the possibility that \( O_2 \) binding is simply occurring at defect sites. Attempts to collect structural data following \( O_2 \) dosing at 473 K revealed that the material was not sufficiently crystalline for a structure determination.

The diffraction data collected for crystals dosed with \( O_2 \) at 298 K were best modeled assuming two crystallographically unique Na\(^+\) or K\(^+\) ion sites. One position is very similar to the cation site near the phenyl groups of the ligand in the reduced, activated structures.\(^{39}\) Indeed, for both \( O_2 \)-dosed structures, the alkali metal ion···phenyl-centroid distances are 3.44(2) \( \text{Å} \), as compared to 3.429(4) \( \text{Å} \) in activated \( \text{Na}_{0.5} \text{Fe}_2 \text{(bdp)}_3 \). The second alkali metal position, with longer alkali metal ion···phenyl-centroid distances of 3.87(2) and 3.88(2) \( \text{Å} \) for sodium and potassium, respectively, appears to stabilize the \( O_2 \) species, with a Na–O distance of 2.30(3) \( \text{Å} \) and a K–O distance of 2.31(3) \( \text{Å} \). The distances between the two crystallographically distinct alkali sites are 1.21(3) \( \text{Å} \) (sodiated structure) and 1.24(3) \( \text{Å} \) (potassiated structure). The \( O_2 \) species and alkali metal ion sites reside near an inversion center at the middle of the triangular pore and are thus duplicated by symmetry. Importantly, the O–O distances of 1.29(6) and 1.34(6) \( \text{Å} \) in the sodiated and potassiated structures, respectively, are consistent with reported bond lengths for superoxo species.\(^{36}\)

The closest pyrazolate \( N \)–\( O \) distances are 5.81(2) and 5.79(2) \( \text{Å} \) for \( A = \text{Na}^+ \) and \( K^+ \), respectively, whereas the corresponding Fe···O distances are 7.16(2) and 7.14(2) \( \text{Å} \). Assuming that outer-sphere electron transfer occurs at a point of closer contact, these relatively large distances between the iron–nitrogen coordination sphere and oxygen atoms imply that substantial rearrangement and movement of the reduced \( O_2 \) species must occur following electron transfer.

We note that both the crystal symmetry and the stoichiometry necessitate partial occupancy of the alkali metal and O atom crystallographic sites. Additional factors, such as structural disorder, the proximity of adsorbed \( O_2 \) to a point of high symmetry in the center of the pore, large thermal motion, and the relatively low electron density of these species, make a precise determination of the O–O bond length and other distances difficult. However, these structures conclusively show the presence of adsorbed \( O_2 \) species and are consistent with an adsorption mechanism involving one-electron reduction of \( O_2 \).

**Analysis of Extra-Framework Species.** Vibrational spectroscopy is often used to probe the nature of reduced \( O_2 \) species given that the bond order and therefore the vibrational frequency of the O–O bond are distinct for \( O_2^- \) and \( O_2^2- \). However, despite numerous attempts, we were unable to assign any \( O=O \) signatures using Raman or even diffuse reflectance infrared spectroscopy (see the Supporting Information for details). We therefore utilized X-ray photoelectron spectroscopy (XPS) and solid-state NMR spectroscopy coupled with density functional theory (DFT) calculations to further elucidate the nature of the \( O_2 \) species adsorbed in A \( \text{Fe}_2 \text{(bdp)}_3 \) and the associated chemical environment of the alkali metal cations.

Because of the strongly bound nature of the \( O_2 \) species in these materials, we were able to directly compare the O 1s signals in \( \text{Fe}_2 \text{(bdp)}_3 \), \( \text{K}_{1.06} \text{Fe}_2 \text{(bdp)}_3 \), and \( \text{K}_{1.06} \text{Fe}_2 \text{(bdp)}_3 \) dosed with 1 bar \( O_2 \) at either 298 or 473 K, under the high vacuum of the XPS measurement chamber. As previously reported,\(^{32}\) \( \text{Fe}_2 \text{(bdp)}_3 \) contains defects likely associated with ligand vacancies. For this material, we observe an O 1s signal that we accordingly assign to oxygen-containing defect species at a binding energy of 531.1 eV (Figure 4), consistent with hydroxides or oxygen-containing organics such as formate.\(^{40–45}\) This peak is also observed at a similar binding energy in \( \text{K}_{1.06} \text{Fe}_2 \text{(bdp)}_3 \), as well as in both \( O_2 \)-dosed \( \text{K}_{1.06} \text{Fe}_2 \text{(bdp)}_3 \) samples. Critically, for both of these \( O_2 \)-dosed samples, a new O 1s peak is also present at a higher binding energy of ~534.1 eV, consistent with a superoxo, rather than more reduced peroxo or oxo species.\(^{40,45,48–48}\) The observation of this new peak for both samples suggests that (i) the nature of the reduced, adsorbed \( O_2 \) species is the same, regardless of dosing temperature, and (ii) the mechanism of \( O_2 \) adsorption is therefore likely also the same. As such, differences in \( O_2 \) adsorption capacity at 298 and 473 K most likely arise from kinetics effects. Furthermore, the relative area of this higher energy peak is greater for the sample dosed with \( O_2 \) at high temperature, as expected given the higher \( O_2 \) loading with increasing temperature. As further corroboration of this signal assignment, we measured the O 1s spectrum of potassium superoxide (KO\(_2\)) and observe a similar binding energy of energy of 533.8 eV (Figure S10).

We turned to solid-state magic-angle spinning (MAS) NMR spectroscopy as a more sensitive probe of local structural
changes occurring upon O₂ dosing and chose to study the Na analogue due to the greater ease of obtaining ²³Na data as compared to ³⁹K NMR data. Typically, NMR spectroscopy of paramagnetic systems is challenging due to hyperfine interactions between unpaired electrons and the NMR-active nucleus. These interactions may be isotropic and through-bond (Fermi contact) and/or anisotropic and through-space (hyperfine dipolar coupling), which often lead to large NMR shifts and highly broadened spectral features.⁴⁹ For example, the highest frequency ²³Na shift of Na₂FePO₄F is 450 ppm, well outside the typical diamagnetic range of −50 to 100 ppm. In this case, unpaired spin density is transferred along bond pathways from the Fe through O and onto Na.⁵⁰ On the other hand, in some paramagnetic systems, the Fermi contact shift may be unusually small due to competition between delocalization and polarization mechanisms. In NaO₂, where superoxide acts as the paramagnetic center, the room-temperature ²³Na shift is only −30 ppm.⁵¹

The ²³Na MAS NMR spectra for activated Na₁.₀₄Fe₂(bdp)₃ and for aliquots of the same sample after dosing with O₂ at 298 K and at 473 K are shown in Figure 5a. Given the large signal width resulting from paramagnetic broadening, data collection required the use of variable-offset cumulative spectroscopy (VOCS), wherein spin echo subspectra are acquired at spaced frequency offsets and summed together.⁵² Two features are consistently observed in these spectra: a relatively sharp feature centered at −12 ppm with associated spinning sideband manifold and a very broad signal centered at −50 ppm, which is somewhat obscured by the first signal. Baseline subtractions of the subspectra were performed to ensure that the intensity of the broad feature was accurate. Moreover, neither signal was observed in control experiments with an empty probe, which confirmed they arose from Na within the sample.

Spectral deconvolutions shown in Figures 5a and S11 strongly suggest that the sharp feature increases and/or the broad feature decreases in intensity with O₂ dosing. For paramagnetic systems, however, observed NMR spectral intensities are generally not quantitative due to rapid spin–lattice (T₁) and spin–spin (T₂) relaxation. For purposes of quantitation, we therefore measured both the ²³Na T₁ and T₂ relaxation times, as shown in Figures S12 and S13. The VOCS spectra are quantitative with respect to T₁ relaxation but not T₂ relaxation. In particular, across all samples, the broad feature has a very short T₂ time (on the order of 500 μs), such that between 35% and 55% of its intensity (depending on the specific sample) is lost prior to acquisition. Correcting the intensity of both deconvoluted signals using the measured T₂ times gives quantitative relative intensities (Figure 5b). The broad feature contributes to 75% of the total spectral intensity for the undosed sample, and the relative intensity of the peak decreases to 61% and 45% in the samples dosed with O₂ at 298 and 473 K, respectively. Conversely, the relative intensity of the sharp component increases from 25% in the activated framework to 39% and 55% in the samples dosed with O₂ at 298 and 473 K, respectively.
These spectral trends imply that the broad feature corresponds to $^{23}$Na sites in the reduced structure that are not interacting with oxygen. The sharp component therefore appears to correspond to a chemically distinct environment associated with incorporated oxygen. Although the chemical shift of the sharp component at $-12$ ppm is in the vicinity of the known room-temperature $^{23}$Na shift of NaO$_2$ ($-30$ ppm), this feature is clearly observed even for the undosed sample and therefore cannot be assigned exclusively to superoxo-associated Na$^+$. We hypothesize that this feature in the undosed spectrum corresponds to Na$^+$ near oxygen-containing ligand-vacancy defects that are clearly observed in the XPS data (for reference, the $^{23}$Na shift of sodium formate is $\sim 0$ ppm). We also expect a smaller degree of spin density transfer from Fe to ligand vacancy sites, and therefore a sharper $^{23}$Na signal for associated Na$^+$ relative to the signal arising from sodium ions in the rest of the framework.

In the O$_2$-dosed samples, then, the sharp feature likely comprises multiple sites, a conclusion supported by analysis of the spinning sideband intensities. In particular, were this feature due only to a single type of Na$^+$ site in the activated framework that becomes more predominant with O$_2$ dosing, the intensity of its spinning sideband manifold should remain proportional to that of the centerband. Instead, the spinning sidebands comprise 65% of the total intensity of this feature in the undosed spectrum but only 48% and 45% of the feature in the spinning sideband intensities. In particular, were this component at $-12$ ppm. However, paramagnetic broadening leading to a fwhm of $\sim 50$ ppm of the sharp component as well as the differing chemical nature of the sodium environment(s) in this system relative to either sodium formate or sodium superoxide mean that deconvolution or distinction by chemical shift alone are not possible, due to likely overlap between the signal observed from Na$^+$ near defects and Na$^+$ near superoxo species.

To corroborate the sign and magnitude of the assigned $^{23}$Na NMR shifts, we performed DFT calculations on a small cluster model (Figure S14) generated from the refined single-crystal structure of the O$_2$-dosed sodiated framework (Figure 1). Many of the linkers were further converted to nonbridging phenyl pyrazolate units to minimize the system size, while still capturing the local sodium ion environments. The calculated isotropic hyperfine coupling constants for the $^{23}$Na sites were found to be small and negative, and by use of the experimental magnetic susceptibility data (see below), they could be further scaled to obtain room-temperature Fermi contact shifts between $-9$ and $-20$ ppm. This shift range is in good agreement with the experimental $^{23}$Na shift of the sharp component at $-12$ ppm, ascribed to Na$^+$ sites near reduced O$_2$ species (and/or defects). These calculations suggest that, despite the highly paramagnetic nature of the framework, the $^{23}$Na nuclei do not experience a significant Fermi contact shift, due to the relatively weak Na$^+$--framework interactions. Moreover, the calculations confirm that the nearby O$_2$ species does not induce large $^{23}$Na Fermi contact shifts. We note that experimental $^{23}$Na NMR characterization of sodium superoxide similarly found the absence of a significant $^{23}$Na Fermi contact shift.

Finally, we performed static and MAS solid-state $^{17}$O NMR spectroscopy after dosing an activated sample of Na$_{1.04}$Fe$_2$(bdp)$_3$ with $^{17}$O-enriched O$_2$ (see the Supporting Information). We did not observe signal in these experiments even after long signal averaging times of $\sim 12$ h, which suggests the speciation of O$_2$ as paramagnetic superoxide rather than diamagnetic peroxide. We note that while $^{17}$O NMR spectra of alkali metal peroxides have been reported, this is not the case for the corresponding superoxides, as the unpaired spin localized on the NMR-active nucleus renders spectral acquisition extremely challenging. Taken together, the $^{23}$Na and $^{17}$O solid-state NMR data support the hypothesis that, upon O$_2$ dosing, the Na$^+$ ions move slightly further from the linkers to accommodate and associate with O$_2$, which is incorporated as a superoxide guest species.

**O$_2$ Adsorption in More-Reduced Fe$_2$(bdp)$_3$ and in an Expanded-Pore Analogue.** Measurable porosity is still observed for O$_2$-dosed K$_{1.09}$Fe$_2$(bdp)$_3$ (Figure S15), which suggests that restricted O$_2$ diffusion—potentially due to pore occlusion by reduced O$_2$ species—does not completely explain the apparent kinetically limited O$_2$ adsorption at ambient temperature. To further investigate the possible restriction of O$_2$ diffusion, we prepared a more reduced form of the framework material, K$_{1.88}$Fe$_2$(bdp)$_3$, as well as an expanded-pore analogue Fe$_2$(bpeb)$_3$ (bpeb$^-$ = 1,4-bis(pyrazolide-4-ylethynyl)benzene) (see below). In the more reduced material, the pores should be even more occluded and O$_2$ diffusion more restricted. Indeed, as noted above, this material is essentially nonporous to N$_2$ at 77 K, with a Langmuir surface area of only $\sim 70$ m$^2$/g (Figure S16). As such, if O$_2$ diffusion represents the primary kinetic barrier to O$_2$ adsorption, it would be expected that the fully reduced material should show far lower O$_2$ uptake.

At 298 K, K$_{1.88}$Fe$_2$(bdp)$_3$ exhibits a steep initial O$_2$ uptake to a loading of 0.68 mmol/g at $\sim 6$ mbar that then tapers off to yield a loading of 0.87 mmol/g at 1 bar (Figure 6). Significantly, for all pressures measured, the O$_2$ capacities are higher than those in the half-reduced material. As was observed for K$_{1.09}$Fe$_2$(bdp)$_3$, the O$_2$ loading at 0.21 bar is far lower than the theoretical capacity of 2.46 mmol/g. However, because this material adsorbs an appreciable quantity of O$_2$, it is unlikely that restricted diffusion is the primary reason for the apparent kinetic control of O$_2$ adsorption. When dosed with O$_2$ at 473 K, K$_{1.88}$Fe$_2$(bdp)$_3$ again exhibits steep uptake with even greater capacities of 1.23, 1.40, and 1.64 mmol/g at 10 mbar, 0.21 bar, and 1 bar, respectively, which suggests the fully reduced framework operates under kinetic limitations similar to those of the half-reduced form. Despite the overall improvement in capacity at elevated temperature, the 1.40 mmol/g uptake (1.13 molecules of O$_2$ per formula unit, Figure S17) in K$_{1.88}$Fe$_2$(bdp)$_3$ near atmospheric oxygen partial pressure is only $\sim 60$% of its theoretical capacity, whereas K$_{1.09}$Fe$_2$(bdp)$_3$ achieves approximately 80% under similar conditions. This result indicates that increased kinetic limitations may occur with increasing reduction above K$_{1.09}$Fe$_2$(bdp)$_3$, such as more restricted movement of cations or sluggish rearrangement of reduced O$_2$ species. Additionally, it is possible that different redox behavior for the fully reduced material to partial formation of more reduced O$_2$ species.
The framework Fe₂(bpeb)_3 features larger interchain separations relative to Fe₂(bdp)_3 (18.2 versus 13.2 Å, respectively; Figure 7), which give rise to larger pores that should reduce or preclude restricted O₂ diffusion. Additionally, this framework displays thermal stability above 350 °C in air, although it is less stable in the presence of water relative to Fe₂(bdp)_3. We prepared H₂bpeb according to reported procedures and synthesized Fe₂(bpeb)_3 in a manner analogous to that of Fe₂(bdp)_3. Notably, we determined a Langmuir surface area of 2270 m²/g for this expanded material (Figure S19), as well as adsorption of O₂ without fusion. Sharp O₂ adsorption occurs in this framework at 298 K until ~5 mbar, corresponding to a loading of 0.52 mmol/g, and loadings of 0.55 and 0.65 mmol/g are achieved close to 0.21 bar and at 1 bar, respectively (Figure 6). At 453 K, 1.9 mmol/g O₂ is adsorbed at 50 mbar and 2.3 mmol/g at 1 bar. Notably, although the 0.55 mmol/g O₂ uptake (0.53 molecules per formula unit) in KₓFe₂(bpeb)_3 at 298 K and ~0.21 bar corresponds to only 26% of its theoretical capacity, at 453 K and ~0.21 bar, the material is capable of adsorbing 95% of its theoretical capacity (1.96 equiv of O₂ per formula unit). These results for the expanded-pore system indicate that there still appears to be some form of kinetic control over the adsorption of O₂ that is almost certainly not associated with restriction of O₂ diffusion. Indeed, if diffusion was the solely limiting factor for O₂ uptake, we would expect the quantity of adsorbed gas to be independent of temperature for Fe₂(bpeb)_3, wherein the large pores should dramatically reduce or eliminate any restriction of diffusion.

Collectively, the reduced forms of Fe₂(bdp)_3 or Fe₂(bpeb)_3 show exceptional selectivity for O₂ at 298 K that only increases at high temperature. The highest O₂ uptake we obtained in the Fe₂(bdp)_3 system at ~0.21 bar O₂ was 1.40 mmol/g at 473 K for K₁.₈₂Fe₂(bdp)_3, as compared to the theoretical capacity for KₓFe₂(bdp)_3 of 2.46 mmol/g. The maximum O₂ capacity at ~0.21 bar O₂ that we measured in the expanded-pore analogue was 2.04 mmol/g at 453 K for K₁.₀₈Fe₂(bpeb)_3, as compared to a theoretical capacity for KₓFe₂(bpeb)_3 of 2.09 mmol/g. To contextualize these results relative to the state-of-the-art, we are not aware of any commercial O₂-selective adsorbents used for air separation. Although the previously mentioned N₂-selective cation-exchanged zeolites have been commercialized, their O₂ output purity is limited, and they must either be regenerated more frequently or used in larger quantities, because N₂ is more abundant than O₂ in air. Several other reported O₂-selective adsorbents exhibit high capacities, but only operate well at temperatures below 298 K, because O₂...
binding is either irreversible or too weak at room temperature. For instance, Fe$_2$(dobic)$_3^{25}$ exhibits a largely reversible uptake of 5.33 mmol/g O$_2$ under 0.21 bar O$_2$ at 226 K, whereas O$_2$ becomes permanently bound at room temperature. On the other hand, although Co$_2$(OH)$_3$(bbta)$_2^{20,30}$ and Co-BTTr$_3^{26}$ adsorb $\sim$4.5 and $\sim$3.3 mmol/g O$_2$, respectively, at 195 K and 0.21 bar O$_2$, they do not show appreciable O$_2$/N$_2$ selectivity at 298 K. Some Cr$^{II}$-based frameworks such as Cr$_3$(btc)$_2$ maintain both stability and high selectivity for O$_2$ at room temperature. To the best of our knowledge, this is the first report of framework materials that maintain both stability and high selectivity for O$_2$ at temperatures as high as 300 K, while allowing for at least partial regeneration and cycling. Importantly, we have not been able to operate at high temperature. To our best knowledge, this is the first report of framework materials that maintain both stability and high selectivity for O$_2$ at temperatures as high as 300 K, while allowing for at least partial regeneration and cycling. Importantly, we have not been able to operate at high temperature. To our best knowledge, this is the first report of framework materials that maintain both stability and high selectivity for O$_2$ at temperatures as high as 300 K, while allowing for at least partial regeneration and cycling. Importantly, we have not been able to operate at high temperature. To our best knowledge, this is the first report of framework materials that maintain both stability and high selectivity for O$_2$ at temperatures as high as 300 K, while allowing for at least partial regeneration and cycling. Importantly, we have not been able to operate at high temperature. To our best knowledge, this is the first report of framework materials that maintain both stability and high selectivity for O$_2$ at temperatures as high as 300 K, while allowing for at least partial regeneration and cycling. Importantly, we have not been able to operate at high temperature.

Electronic and Magnetic Properties of KFe$_2$(bdp)$_3$ and O$_2$-Dosed KFe$_2$(bdp)$_3$. To further examine O$_2$ adsorption behavior in chemically reduced Fe$_2$(bdp)$_3$, we turned to a combination of $^{57}$Fe Mössbauer spectroscopy and magnetic susceptibility measurements. Mössbauer analysis has been used previously to confirm the increasing presence of high-spin Fe$^{III}$ centers as well as a high degree of electron delocalization with increased chemical reduction of Fe$_2$(bdp)$_3$. The 5 K Mössbauer spectrum for a sample of K$_{1.06}$Fe$_2$(bdp)$_3$ dosed with O$_2$ at 473 K (i.e., the most oxidized, O$_2$-rich sample) reveals two distinct Fe environments (Figure 8). The primary spectral feature has an isomer shift of 0.129(2) mm/s that matches the shift for Fe$_2$(bdp)$_3$ (Fe$^{III}$, $\langle \delta \rangle = 0.129(1)$ mm/s) and is distinct from the shift for K$_{1.1}$Fe$_2$(bdp)$_3$ (Fe$^{II}$, $\langle \delta \rangle = 0.214(5)$ mm/s). This result indicates that the introduction of O$_2$ causes electron transfer from the reduced framework, which results in reoxidation of the iron centers back to low-spin Fe$^{III}$. The isomer shift of the second feature is 0.42(2) mm/s, which is considerably lower than the value reported for Fe$^{II}$ in K$_{1.1}$Fe$_2$(bdp)$_3$, and is indicative of a new electronic environment. The exact nature of this species remains unclear, but the signal could correspond to remnant low-spin Fe$^{II}$. Another assignment consistent with this second feature is high-spin Fe$^{III}$. In either case, interactions between pore-dwelling superoxo species and the framework may also contribute to the observed signal parameters. The full assignment of this signal and complete understanding of the complex electronic and magnetic structure in either reduced Fe$_2$(bdp)$_3$ or its O$_2$-dosed congeners are beyond the scope of this work, but a more detailed discussion of the Mössbauer measurements can be found in the Supporting Information.

Figure 8. The 5 K Mössbauer spectrum for a sample of K$_{1.06}$Fe$_2$(bdp)$_3$ dosed with 1 bar O$_2$ at 473 K. The red and blue doublet fits correspond to low-spin Fe$^{III}$ and a previously unobserved Fe species, respectively.

The Mössbauer spectrum for K$_{1.06}$Fe$_2$(bdp)$_3$ dosed with O$_2$ at ambient temperature is very similar (Figure S25), as it displays two distinct features with isomer shifts and quadrupole splittings similar to those for the sample dosed at 473 K. Both data sets indicate that K$_{1.1}$Fe$_2$(bdp)$_3$ is substantially reoxidized in the presence of O$_2$ and features a new iron electronic environment. Given the paramagnetic nature of both the framework and the observed superoxo species, we further investigated the electronic structure of activated and O$_2$-dosed samples of K$_{1.1}$Fe$_2$(bdp)$_3$ using magnetic susceptibility measurements (Figure 9). At 300 K, the value of the molar magnetic susceptibility times temperature ($\chi_M T$) versus T obtained at 7 T for Fe$_2$(bdp)$_3$ (black), K$_{1.06}$Fe$_2$(bdp)$_3$ (blue), and K$_{1.06}$Fe$_2$(bdp)$_3$ dosed with 1 bar of O$_2$ at 298 K (red) and 473 K (dark red).

Figure 9. Variable-temperature molar magnetic susceptibility times temperature ($\chi_M T$) versus T obtained at 7 T for Fe$_2$(bdp)$_3$ (black), K$_{1.06}$Fe$_2$(bdp)$_3$ (blue), and K$_{1.06}$Fe$_2$(bdp)$_3$ dosed with 1 bar of O$_2$ at 298 K (red) and 473 K (dark red).
clusters of low-spin Fe$^{III}$ centers strongly coupled by conduction electrons, although further measurements are needed to understand fully the magnetic structure of this material.

Both the ambient-temperature and the high-temperature O$_2$-dosed samples exhibit lower $\chi_M T$ values of 1.74 and 2.03 emu·K/mol, respectively, as compared to the activated sample (Figure 9), consistent with the removal of conduction electrons upon electron transfer to adsorbed O$_2$. Importantly, the larger $\chi_M T$ value of the high-temperature dosed sample is consistent with an increased concentration of S = 1/2 superoxo species within the pores of the framework. Indeed, the room-temperature $\chi_M T$ value of this sample is 0.29 emu·K/mol larger than the room temperature moment of Fe$_2$(bdp)$_3$ reasonably close to the expected increase of 0.32 emu·K/mol, when one assumes one S = 1/2 spin per adsorbed O$_2$ and no change in the moment of the host framework. Unfortunately, quantitative analysis of the magnetic susceptibility of these samples is complicated by contributions from temperature-independent paramagnetism (Figure S29), even under an applied field of 7 T, as was previously observed for Fe$_2$(bdp)$_3$. However, the data qualitatively agree with the formation of an S = 1/2 superoxo species upon adsorption of O$_2$.

O$_2$ Adsorption Mechanism. The foregoing results from gas adsorption, X-ray diffraction, spectroscopic, and magnetic susceptibility experiments provide a consistent picture for the mechanism of O$_2$ adsorption in these chemically reduced Fe$^{III}$-pyrazolate frameworks. Upon introduction of O$_2$ even at very low pressures, the strongly reducing framework drives what is ostensibly outer-sphere electron transfer, and thereby reduces O$_2$ to a superoxide (O$_2^{-}$) guest species, followed by movement of this reduced species to a more favorable binding position stabilized by the alkali metal cations residing within the pores. The theoretical O$_2$ uptake expected for this mechanism is not realized at 298 K due to a kinetic limitation. This kinetic limitation is almost certainly not due to the restriction of O$_2$ diffusion resulting from pore occlusion by reduced O$_2$ species. Instead, it is likely a result of a large reorganization energy associated with rearrangement of the alkali cations from their preferred positions prior to O$_2$ dosing and/or the movement and ordering of superoxo species after O$_2$ reduction. This explanation seems especially plausible when considering the crystal structures of the O$_2$-loaded frameworks. The alkali metal cation sites that stabilize the O$_2$ species are over 1.2 Å away from the other alkali metal sites that interact with the ligand phenyl rings, and the reduced O$_2$ species are positioned relatively far away from the iron centers. These distances imply large degrees of rearrangement after reduction of O$_2$ and suggest that back-transfer of electrons from the reduced O$_2$ species to the framework may also be subject to such a barrier, which would impose significant thermal energy requirements for framework regeneration. One possible approach to enhance the cycling ability of the material would thus be to employ cations that could enhance O$_2$ reduction by positioning reduced O$_2$ species much closer to the framework. These templating cations might also facilitate the reversal of this reduction.

CONCLUSION

Molecular complexes and materials such as metal–organic frameworks that reversibly bind dioxygen traditionally do so at coordinatively unsaturated, redox-active metal sites, which transfer an electron to O$_2$ by an inner-sphere mecha-

nism.$^{9,12,23–30}$ Here, we have presented an alternative strategy for the selective capture of O$_2$ via outer-sphere electron transfer to O$_2$ from a robust, chemically reduced framework with coordinatively saturated, redox-active metal sites. Through a suite of characterization techniques, we have shown that the O$_2$ species adsorbed in A$_x$Fe$_2$(bdp)$_3$ (A = Na$^+$, K$^+$) are superoxide moieties stabilized by sodium or potassium cations. The deeper understanding gained here of a relatively unexplored mechanism of O$_2$ reduction and binding is of fundamental interest; yet these results can also inform the design of new O$_2$ selective adsorbents for numerous industries and important pre- and post-combustion carbon capture technologies that require high-purity oxygen.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c06570.

Synthesis and characterization details, and details of gas adsorption, spectroscopic, and diffraction measurements and analysis (PDF)
X-ray crystallographic information for Na$_{1.5}$Fe$_2$(bdp)$_3$ (CIF)
X-ray crystallographic information for K$_{0.74}$Fe$_2$(bdp)$_3$ (CIF)

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Notes
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