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Novel Metal-Organic Frameworks for Efficient Stationary Sources via Oxyfuel Combustion

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Abstract

Oxy-fuel combustion is a well-known approach to improve the heat transfer associated with stationary energy processes. Its overall penetration into industrial and power markets is constrained by the high cost of existing air separation technologies for generating oxygen. Cryogenic air separation is the most widely used technology for generating oxygen but is complex and expensive. Pressure swing adsorption is a competing technology that uses activated carbon, zeolites and polymer membranes for gas separations. However, it is expensive and limited to moderate purity O_2. MOFs are cutting edge materials for gas separations at ambient pressure and room temperature, potentially revolutionizing the PSA process and providing dramatic process efficiency improvements through oxy-fuel combustion. This LDRD combined (1) MOF synthesis, (2) gas sorption testing, (3) MD simulations and crystallography of gas siting in pores for structure-property relationship, (4) combustion testing and (5) technoeconomic analysis to aid in real-world implementation.

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CONTENTS

NOMENCLATURE

Å	angstrom
ANL	Argonne National Laboratory
ARPA-E	Advanced Research Projects Agency - Energy
BNL	Brookhaven National Laboratory
CO_2	carbon dioxide
Cu-BTC	copper benzene-1,3,5-tricarboxylate MOF
HKUST-1	commercial MOF "Basolite C300"
g	gram
GA Tech	Georgia Institute of Technology
K	Kelvin
kHz	kilo hertz
LDRD	Laboratory Directed Research and Development program
LII	laser-induced incandescence
m	meter
MD	molecular dynamics
MOF	metal-organic framework
N_2	nitrogen
NOx	generic term for nitric oxide (NO) and nitrogen dioxide (NO_2)
NETL	National Energy Technology Laboratory
NREL	National Renewable Energy Laboratory
O_2	oxygen
PSA	pressure swing adsorption
PNNL	Pacific Northwest National Laboratory
DOE	Department of Energy
SNL	Sandia National Laboratories

1. INTRODUCTION

In this Laboratory Directed Research and Development (LDRD) project, we used an integrated approach of modeling, synthesis/characterization, combustion and systems analysis studies to develop highly selective and high surface area metal-organic frameworks (MOFs) for improved efficiencies in oxy-fuel combustion processes. Oxygen-enriched combustion, or full oxy-fuel combustion, are well-known approaches to improve the heat transfer associated with stationary energy processes utilized by heavy industry or in power production.[1,2] The addition of oxygen results in higher thermal efficiency, greater flame stability, improved ignition characteristics, greater burner turndown ratio, improved fuel flexibility, and reduced exhaust gas volumes, all stemming from the reduction or elimination of the N_2 component of air. In addition, NO_x emissions can be nearly completely eliminated in oxy-fuel combustion. Finally, oxy-fuel combustion offers a lower-cost route to CO_2 capture, for either subsequent utilization (such as in enhanced oil recovery) or geologic sequestration. While the glass-melting industry, aluminum industry, and steel-making industry have adopted oxy-fuel combustion into some of their operations, its overall penetration into industrial and power markets is currently constrained by the high cost of existing air separation technologies for generating oxygen.

The major advantage of oxy-fuel combustion to thermal processes is through the much greater radiant emission from these flames. The radiant emission increases because of the higher flame temperatures associated with oxygen-enrichment (up to nearly 3000 K) and because the flame gases themselves have a much greater emissivity – absent the dilution from N_2 associated with traditional air-based combustion, the concentrations of radiantly active combustion products are 3.5 times larger in oxy-fuel flames. Careful tailoring of oxy-fuel flames allows the formation of enhanced soot levels within the flame, increasing thermal radiation (while still burning out soot and avoiding soot emissions). Radiation has been shown to cause 98% of the heat transfer from oxy-fuel flames to the 'batch' in glass-melting furnaces.[2] Improvements in furnace efficiency when retrofitting air-fired furnaces to oxy-fired have ranged from 20-60% in glass and steel heating furnaces.[3-5]

Cryogenic air separation is the most widely used technology for generating large flows of oxygen. This approach generates oxygen with a purity of 90-99.5% and can scale to large production sizes. Unfortunately, it is a complex and expensive technology, in terms of both capital cost and energy consumption. Pressure swing adsorption (PSA) is a competing technology, but is currently constrained to applications that do not require oxygen purity greater than 94%. Existing PSA systems generally consist of a six-step batch production process with significant capital cost. The separations materials most commonly used in the PSA process[1] are activated carbon (with high surface area), zeolites (high surface area, size selective porosity) and polymer membranes at ambient temperature, and ceramic membranes[6] at high temperatures (low volume applications). Improved oxygen separations materials that can be used at ambient pressure and room temperature (RT) will translate into a higher energy efficiency PSA process. MOFs are the cutting edge materials needed for dramatic improvements to oxy-fuel combustion.

Our proposed study into novel porous MOFs for highly selective O_2 sorption focuses on a precise design strategy of high tunability and modularity via both the inorganic and organic components of the framework. MOFs are of great interest in this application as they have very high surface areas (>1000m^2/g), crystalline defined pores (some with zeolitic characteristic size selectivity), and can have designed/tuned features that enhance both chemisorption and physisorption of select gas molecules. We will explore these tuned features in this project through guest-host interaction modeling, synthesis design, and guest-host crystallographic determination combined with single and mixed gas sorption studies.

Though not extensive, there was some preliminary MOF for O_2 separations data in the literature.[1,7] Specifically, it was done at low temperature (77K), or with MOFs with small enough pore openings for molecular sieving abilities (kinetic diameter O_2 = 3.46Å, vs. the larger N_2 = 3.64 Å) for O_2/N_2 separations.[8,9] In studies with high surface area MOFs with large pore openings, the separations were dictated by the differences in magnetic susceptibilities and sorption dynamics for enhanced O_2 affinity at room temperature.[10] More recently, a few studies with only single gas streams focused on the use of MOFs for air purification for oxy-fuel combustion.[11-13] Favorable separations using MOFs closer to RT were obtained when testing MOFs with coordinatively unsaturated metal centers as binding sites for O_2.[11] High theoretical

O_2/N_2 selectivities were calculated (up to 38) from single component isotherms.[12] Furthermore, our team currently works on MOFs for single,[14] and complex stream, gas sorptions.

Integration of the *MOF research* with *combustion testing and analysis* addresses two important questions for process industries: (1) how much enhancement in radiative heating is possible with oxygen-enriched combustion at different levels of oxygen enrichment, and (2) how can oxygen-enriched burners be effectively designed to maximize radiant emission. Building off of earlier studies into the physical characteristics and NO_x emission trends of oxygen-enriched flames,[15] we focused on the impact of oxygen-enrichment on radiant emission. We also conducted technoeconomic analysis that quantified how the enhanced radiant emission from the flame translates into overall process efficiency increases. Whereas previous oxy-fuel combustion research was not been able to distinguish between radiant emission from soot and that from gas species,[16] we are able to do so by a novel combination of laser diagnostics and radiant emission analysis.

We successfully accomplished much of what we intended in this 3 year Laboratories Directed Research and Development (LDRD) program at Sandia National Laboratories. This report will serve as a summary of the accomplishments from the program. The general topic areas covered include: modeling of binding energies of MOF metal centers to O_2 or N_2 gas molecules; the synthesis of MOFs with different metal centers, based on modeling predictions and enhanced O_2/N_2 selectivities; soot formation studies based on novel burner designs and variable O_2 concentration in flame; and flame imaging. Much of this LDRD research has been published in peer reviewed articles. Therefore, we have only included brief summaries of the work in this report and reference it appropriately. The following research successes are highlighted herein: (1) DFT and experimental effects of metal in MOFs for O_2/N_2 separations, (2) enhanced O_2 selectivity versus N_2 by partial metal substitution in MOFs, (3) soot formation and its impact on flame radiation during turbulent oxygen enriched combustion of methane, and (4) the effects of repetitive pulsing on multi-kHz planar laser-induced incandescence imaging in laminar and turbulent flames.

2. RESULTS

2.1 DFT and Experimental effects of Metal in MOFS for O_2/N_2 separations

Computational screening of metal−organic framework (MOF)materials for selective oxygen adsorption from air is used to identify newsorbents for oxyfuel combustion process feedstock streams. A comprehensivestudy on the effect of MOF metal chemistry on gas binding energies in twocommon but structurally disparate MOFs has been undertaken. Dispersion-corrected density functional theory (DFT) methods were used to calculatethe oxygen and nitrogen binding energies with each of 14 metals, respectively,substituted into two MOF series, M_2(dobdc) and $M_3(btc)_2$. The accuracy ofDFT methods was validated by comparing trends in binding energy withexperimental gas sorption measurements. A periodic trend in oxygen bindingenergies was found, with greater oxygen binding energies for early transition-metal-substituted MOFs compared to late transition metal MOFs; this wasindependent of MOF structural type. The larger binding energies wereassociated with oxygen binding in a side-on configuration to the metal, withconcomitant lengthening of the O−O bond. In contrast, nitrogen binding energies were similar across the transition metal series, regardless of both MOF structural type and metal identity. Taken together, these findings suggest that early transition metal MOFs are best suited to separating oxygen from nitrogen and that the MOF structural type is less important than the metal identity.

A detailed description of the experiments and results can be found in the recently published paper, see reference 17.

2.2 Enhanced O_2 Selectivity versus N_2 by Partial Metal Substitution in MOFs

Here, we describe the homogeneous substitution of Mn,Fe, and Co at various levels into a prototypical metal−organicframework (MOF), namely Cu-BTC (HKUST-1), and the effect ofthat substitution on preferential gas sorption. Using a combination ofdensity functional theory (DFT) calculations, postsynthetic metalsubstitutions, materials characterization, and gas sorption testing, wedemonstrate that the identity of the metal ion has a quantifiable effecton their oxygen and nitrogen sorption properties at cryogenictemperatures. An excellent correlation is found between O_2/N_2selectivities determined experimentally at 77 K and the difference inO_2 and N_2 binding energies calculated from DFT modeling data: Mn > Fe ≈ Co ≫ Cu. Room temperature gas sorption studies were also performed and correlated with metal substitution. The Fe-exchanged sample shows a significantly higher nitrogen isosteric heat of adsorption at temperatures close to ambient conditions (273−298 K) as compared to all other metals studied, indicative of favorable interactions between N_2 and coordinatively unsaturated Fe metal centers. Interestingly, differences in gas adsorption results at cryogenic and room temperatures are evident; they are explained by comparing experimental results with DFT binding energies (0 K) and room temperature Grand Canonical Monte Carlo simulations.

A detailed description of the experiments and results can be found in the recently published paper, see reference 18.

2.3 Soot Formation and its Impact on Flame Radiation during Turbulent, Non-Premixed Oxygen-Enriched Combustion of Methane

Non-premixed oxy-fuel combustion of natural gas is used in many important industrial applications where high-intensity heat is required, such as glass manufacturing and metal forging and shaping. In these applications, the high flame temperatures achieved by oxy-fuel increases radiative heat transfer to the surfaces of interest and soot formation within the flame is desired for further augmentation of radiation. However, the high energy consumption and overall economics of oxygen production have limited the penetration of oxy-fuel combustion technologies. New approaches to oxygen production, using ion transport membranes or metal organic frameworks (MOFs), are being developed which may reduce the oxygen production costs associated with conventional cryogenic air separation, but which are likely to be more economical for intermediate levels of oxygen enrichment of air, rather than for the nearly complete oxygen separation that occurs with cryogenic separation.

To determine the influence of intermediate levels of oxygen enrichment on soot formation and radiation, we have developed a non-premixed coannular burner in which oxygen concentrations and flow rates are independently varied, in an attempt to separate the effects of turbulent mixing intensity, characteristic flame residence time, and oxygen enrichment on soot formation and flame radiation intensity. Local radiation intensities and soot concentrations have been measured using a thin-film thermopile and laser-induced incandescence, respectively. Results show that turbulence intensity has a marked effect on both soot formation and flame radiation. Somewhat surprisingly, soot formation is seen to increase as the oxygen concentration falls from 100%, for flames in which the turbulence intensity stays the same. Coincidentally, the thermal radiation from such flames with constant mixing intensity stays constant for an extended range of oxygen concentrations before gradually decreasing. These results suggest that properly designed oxygen-enriched burners may be able to achieve virtually identical thermal radiation intensities as traditional oxy-fuel burners utilizing high-purity oxygen.

A detailed description of the experiments and results can be found in the recently published paper, see reference 19.

2.4 Effects of Repetitive Pulsing on Multi-kHz Planar Laser-Induced Incandescence Imaging in Laminar and Turbulent Flames

Planar laser-induced incandescence (LII) imaging is reported at repetition rates up to 100 kHz using a burst-mode laser system to enable studies of soot formation dynamics in highly turbulent flames. To quantify the accuracy and uncertainty of relative soot volume fraction measurements, the temporal evolution of the LII field in laminar and turbulent flames is examined at various laser operating conditions. Under high-speed repetitive probing, it is found that LII signals are sensitive to changes in soot physical characteristics when operating at high laser fluences within the soot vaporization regime. For these laser conditions, strong planar LII signals are observed at measurement rates up to 100 kHz but are primarily useful for qualitative tracking of soot structure dynamics. However, LII signals collected at lower fluences allow sequential planar measurements of the relative soot volume fraction with sufficient signal-to-noise ratio at repetition rates of 10–50 kHz. Guidelines for identifying and avoiding the onset of repetitive probe effects in the LII signals are discussed, along with other potential sources of measurement error and uncertainty.

A detailed description of the experiments and results can be found in the recently published paper, see reference 20.

3. CONCLUSION

Oxy-fuel combustion is a well-known approach to improve the heat transfer associated with stationary energy processes. However, its overall penetration into industrial and power markets is constrained by the high cost of existing air separation technologies for generating oxygen. Cryogenic air separation is the most widely used technology for generating large flows of oxygen but is a complex and expensive technology. Pressure swing adsorption (PSA) is a competing technology that uses separations materials such as activated carbon, zeolites and polymer membranes. Current PSA technology is expensive and limited to moderate purity O_2 applications because of limitations of existing separations materials. MOFs are cutting edge materials for gas separations at ambient pressure and room temperature, potentially revolutionizing the PSA process and providing dramatic process efficiency improvements through oxy-fuel combustion. This LDRD produced fundamental knowledge on novel MOFs for gas separations and the appropriate burner designs and operations that will be leveraged to applied studies and/or commercialization of new oxy-fuel processes.

Our project was both an innovative approach for developing novel high selectivity MOFs for O_2 purification and was cutting edge for (1) optimized MOF synthesis, (2) testing of preferred O_2 sorption from multicomponent streams, (3) combined MD simulations and crystallography of gas siting in pores for structure-property relationship studies, (4) combustions testing and (5) systems analysis to aid in real-world implementation.

The breakthrough research herein bridged discovery/fundamental science to domestic energy production while addressing National Challenges such as reducing our dependence on foreign oil and increasing our use of low carbon power generation. In particular, the success of the results herein will aid in reducing U.S. industrial energy use and CO_2 emissions.

With that in mind, we have pursued continuation funding for the program through various DOE offices. These include proposals submitted to ARPA-E and NETL/FE (each with GA Tech and Inmondo Inc), and DOE/Fuel Cell Technologies (a consortium including PNNL, SNL, NREL, BNL, ANL). To date, we have not been successful in new funding opportunities. However, we continue to look for new avenues to bring these research successes into future programs.

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