



Amine–Oxide Hybrid Materials for CO₂ Capture from Ambient Air

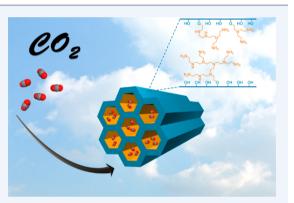
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Supporting Information

CONSPECTUS: Oxide supports functionalized with amine moieties have been used for decades as catalysts and chromatographic media. Owing to the recognized impact of atmospheric CO_2 on global climate change, the study of the use of amine-oxide hybrid materials as CO_2 sorbents has exploded in the past decade. While the majority of the work has concerned separation of CO_2 from dilute mixtures such as flue gas from coal-fired power plants, it has been recognized by us and others that such supported amine materials are also perhaps uniquely suited to extract CO_2 from ultradilute gas mixtures, such as ambient air. As unique, low temperature chemisorbents, they can operate under ambient conditions, spontaneously extracting CO_2 from ambient air, while being regenerated under mild conditions using heat or the combination of heat and vacuum.



This Account describes the evolution of our activities on the design of amine-functionalized silica materials for catalysis to the design, characterization, and utilization of these materials in CO_2 separations. New materials developed in our laboratory, such as hyperbranched aminosilica materials, and previously known amine-oxide hybrid compositions, have been extensively studied for CO_2 extraction from simulated ambient air (400 ppm of CO_2). The role of amine type and structure (molecular, polymeric), support type and structure, the stability of the various compositions under simulated operating conditions, and the nature of the adsorbed CO_2 have been investigated in detail. The requirements for an effective, practical air capture process have been outlined and the ability of amine–oxide hybrid materials to meet these needs has been discussed. Ultimately, the practicality of such a "direct air capture" process is predicated not only on the physicochemical properties of the sorbent, but also how the sorbent operates in a practical process that offers a scalable gas–solid contacting strategy. In this regard, the utility of low pressure drop monolith contactors is suggested to offer a practical mode of amine sorbent/air contacting for direct air capture.

INTRODUCTION

With scientific consensus that anthropogenic CO₂ emissions are a major contributor to global climate change has come intense interest in scientific and engineering communities in the capture of CO₂ from combustion processes for subsequent sequestration and utilization. A variety of technologies have been considered for postcombustion CO₂ capture, with aqueous amine absorption being the most mature, and solid adsorption and membrane processes under rapid development. Postcombustion capture is typically only considered from large point sources, such as coal or gas-fired power plants, or large industrial sources that produce large volumes of CO₂ (though often in relatively dilute mixtures of 5-20% CO₂ by volume). However, these point sources, while accounting for large volumes of CO₂, typically only account for one-third to onehalf of anthropogenic CO2 emissions. The challenge of developing a technology that could allow for capture of CO₂ from all emissions sources led, in part, to the development of approaches to extract CO₂ from ambient air, referred to as "direct air capture" (DAC) in this Account. The early

development of technologies for DAC has previously been reviewed by us. $\!\!\!\!$

While the idea of developing materials or processes to remove CO_2 from ambient air has been described in the literature for at least 70 years, several seminal publications by Lackner in 1999 brought the concept to light as a means of potentially combatting climate change.^{2,3} The ability to reduce CO_2 concentrations in air in confined environments has also long been important in space travel and in submarines, and in the oil crises of the 1970s, was considered as a way to generate carbon feedstocks to make fuels. Following Lackner's initial reports of absorption based approaches for CO_2 capture from ambient air, other air capture pioneers such as Keith began developing hypothetical air capture processes.⁴ Only in the past decade has the field of direct air capture started to grow rapidly, with many materials researchers now studying the adsorption of

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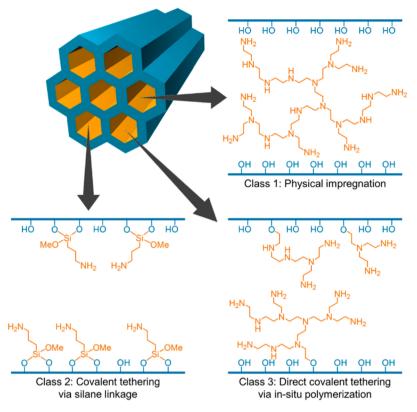


Figure 1. Representation of the three classes of amine adsorbent materials.

 CO_2 on solids at ultralow concentrations (ca. 400 ppm) that are relevant to CO_2 extraction from the ambient air.⁵

SUPPORTED AMINE MATERIALS FOR CATALYSIS AND CO₂ CAPTURE

The most well-studied materials for DAC applications today are solid-supported amines. Our initial foray into the design of supported amines targeted a different purpose—the design of supported organometallic catalysts.^{6–11} This work equipped our laboratory with the ability to create different oxide-supported amines with different distributions of amine sites. We have continued to work extensively on catalysis with supported amines, with a strong emphasis on their use as Lewis basic organocatalysts.^{12–14}

Our initial work preparing well-defined aminosilica materials led to a Department of Energy (DOE) funded program on the design of new supported amine materials for CO₂ capture from flue gas, where we worked with researchers at the National Energy Technology Laboratory (NETL). Seeking to create a new method for preparing silica-supported amine materials that was both (i) simple and scalable and (ii) yielded materials with large densities of amine sites that carried with them large CO₂ adsorption capacities, we synthesized a class of materials referred to as hyperbranched aminosilica materials (HAS), prepared via the in situ polymerization of aziridine¹⁵ on/in mesoporous silica supports.¹⁶ This approach had been previously used to functionalize the silica surface of a flat, silicon wafer,¹⁷ and we adapted it to the use of porous silica materials. In parallel with our work, another group developed similar materials, though without an application.¹⁸ In 2012, we were granted a broad composition of matter patent on these materials.¹⁹ This approach offers significant versatility in creating functional amine-oxide composite materials for CO2

capture from dilute gas streams, as a variety of strained amine macrocycles can be used, including aziridine and azetidines, and the amine loading can be controlled via the reaction stoichiometry employed in the synthesis. Furthermore, the synthesis can be carried out in the vapor phase as well.²⁰ High CO₂ saturation capacities were obtained at high amine loadings, though the equilibration times for materials at high amine loadings can be quite long. This is due to the nature of the synthesis, whereby highly reactive monomers that can react with either the oxide surface or a propagating chain end are used, resulting in polymerization (under some conditions, preferentially) at pore openings, thereby blocking pores at high amine loadings.²¹ Work continues developing supported amine materials, both HAS materials^{20–22} (which we refer to as class 3 amine sorbents), as well as more traditional supported amine materials based on impregnation of presynthesized amine molecules or macromolecules (referred to as class 1 sorbents)²³ and materials prepared by covalently linking amine moieties to the support material, often using organosilanes (referred to as class 2 sorbents), 24,25 for postcombustion capture of CO₂. A review of supported amine materials for applications in carbon capture, along with the above sorbent class designations (Figure 1) was published in 2011.²⁶

SUPPORTED AMINE MATERIALS FOR CO₂ CAPTURE FROM AIR

In 2008, we started working with a start-up company, Global Thermostat LLC, with the challenge of designing adsorbents that could effectively remove CO_2 directly from ambient air. For this application, concentrating an ultradilute mixture (air contains about 400 ppm of CO_2 today) near ambient conditions, it was clear that a chemisorbing material, with strong surface– CO_2 interactions, would be needed. Further-

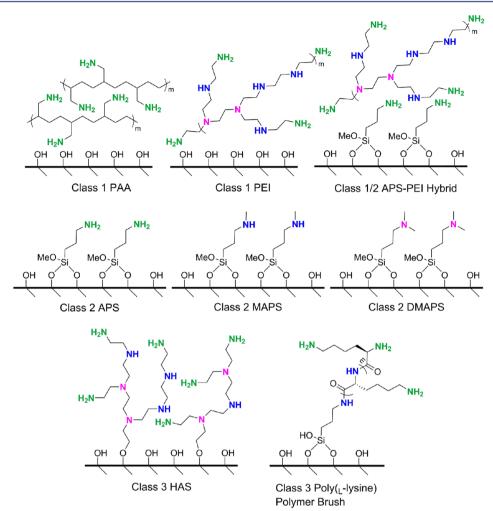


Figure 2. Amine-oxide materials investigated for DAC applications in the Jones group.

more, the material would ideally operate at low temperatures, near ambient conditions, and be effective in all humidity conditions. Recognizing that supported amine materials are rare examples of low temperature chemisorbents and that they are likely lower cost and more easily prepared at scale than metalorganic frameworks (MOFs) or covalent-organic frameworks (COFs) in the short term, we focused our attention on oxidesupported amine materials for DAC applications. This included significant efforts exploring the use of class 1, 2, and 3 materials for CO₂ adsorption from ultradilute gases. Our initial hypothesis was that the high heat of adsorption associated with chemisorbents would yield a steep adsorption isotherm at low CO₂ partial pressures, leading to good uptakes under air capture conditions. Given this hypothesis, we first disclosed the use of hyperbranched aminosilica materials for CO₂ capture from ambient air in 2009 at the AIChE Annual Meeting. Around this time, the development of such materials in academic laboratories across the globe began to take off in earnest, with Sayari et al. publishing on the use of class 2 aminosilica materials in 2010²⁷ followed by the reports using amine sorbents from us^{28-32} as well as the groups of Steinfield,^{33,34} Yang,³⁵ and Olah³⁶ in 2011.

The first materials we described for CO_2 extraction from ambient air were class 3 HAS materials. A series of HAS materials whereby poly(ethylenimine) (PEI) was polymerized on mesoporous SBA-15 silica supports to achieve different amine loadings (0-42 wt % aminopolymer) was prepared and evaluated for CO₂ capture from both dry and humid, simulated flue gas (10% CO₂) and simulated air (400 ppm of CO₂).²⁸ While the gas composition varied by a factor of 250, we showed that the pseudoequilibrium CO_2 capacities varied only by a factor of 2.2-8.5. This clearly demonstrated that the use of amine-based, low temperature chemisorbents could allow for effective concentration of CO₂ from even ultradilute sources such as ambient air. However, there was a trade-off between saturation capacity and adsorption kinetics that was directly correlated with amine loading. While high amine loading materials achieved the best pseudoequilibrium capacities (~1.7 mol CO_2/kg sorbent for the highest amine loading material; 42 wt % aminopolymer), this material also had the longest equilibration time due to the strong diffusional limitations present in the polymer-filled pores of this first generation material. This trade-off illustrates a key challenge for any material in a practical adsorption process, as multiple factors must be balanced, as discussed in more detail further below.

Following our initial disclosure of HAS materials for DAC, we explored a variety of different sorbent compositions for adsorption of CO_2 from ultradilute mixtures. One such contribution, also disclosed in 2011, was the use of class 1 aminosilica materials composed of commercially available low molecular weight PEI impregnated into porous silicas.²⁹ Class 1 aminosilica materials, which lack covalent bonds linking the

amines to the support, as found in class 2 and class 3 materials, have many advantages, including ease of preparation and large amine loadings.^{26,37} Some of the materials in this study were prepared by our collaborator, McMahan Gray, at NETL, and then characterized and evaluated for CO_2 capture from simulated air in our laboratory. High CO_2 capacities were achieved, exceeding those of the HAS materials mentioned above. Additionally, hybrid class 1/2 sorbents were also developed in this work, whereby the silica was functionalized with an aminosilane, as in class 2 sorbents, and commercial PEI, as in class 1 sorbents.²⁹ These hybrids offered enhanced stability over several cycles. Similar hybrids were subsequently evaluated by others for CO_2 capture from simulated flue gases.³⁸

That same year, we also explored the use of alternate class 3 sorbents originally developed by Shantz and Lunn³⁹ for CO₂ capture from simulated ambient air. These materials were based on the polymerization of Z-protected L-lysine N-carboxyanhydride on an aminopropyl-functionalized SBA-15 support. This approach resulted in polymer brushes tethered to the oxide surface within the mesoporous silica network, yielding a hybrid aminosilica rich in primary amine groups. Figure 2 provides an illustration of this material along with other amine sorbents studied by our group. The pseudoequilibrium CO₂ capacities achieved were moderate compared to the above two reports owing to the lower amine loadings achieved. However, the amine efficiencies (mol CO₂ captured/mol amine group) under dry conditions for comparable amine loadings compared well with the state-of-the-art at that time (0.12).³⁰

Given that our initial work explored the use of branched PEIbased aminopolymers, which contain a mixture of primary, secondary, and tertiary amines, for direct air capture of CO₂, we next sought to evaluate each amine type in isolation. In that work, a series of mesoporous silicas functionalized with only primary (3-aminopropylsilyl, APS), secondary (N-methyl-3aminopropylsilyl, MAPS), or tertiary (N,N-dimethyl-3-aminopropylsilyl, DMAPS) amines grafted to the support were prepared and characterized.⁴⁰ Adsorption isotherms were measured under dry conditions for these class 2 aminosilica materials, which all had similar amine loadings on a common silica support, with a specific focus on the ultralow pressure regime important to direct air capture. The results clearly demonstrated that primary amines offered the highest potential for CO_2 capture under such conditions, with secondary amines offering much lower capacities at similar amine loadings. Tertiary amines were not useful, as anticipated based on the proposed carbamate structure of the adsorbed CO₂ under dry conditions.^{26,37} Based on isotherms obtained at multiple temperatures, the isosteric heats of adsorption at zero coverage were estimated from the primary and secondary amines containing materials, with estimates of 112 and 84 kJ/mol, respectively. These results initially suggested that primary amines yielded a material with a steeper isotherm at low pressures due to a higher enthalpy of reaction of the primary amine with CO₂ relative to secondary amines. However, followup work in our laboratory whereby the heats of CO₂ adsorption were directly measured calorimetrically demonstrated that aliphatic primary and secondary amines have similar reaction enthalpies of approximately 90 kJ/mol with CO2. This suggested that it is favorable entropic factors as opposed to enthalpic contributions that make primary amines more effective at adsorbing CO₂ under DAC conditions.⁴¹

At the 2012 Frontiers of Engineering Symposium, Jones presented an overview of the possible use of DAC for large scale CO₂ removal from the atmosphere in a session on geoengineering. In this discussion, five key needs were outlined to enable the development of potentially cost-effective DAC processes.⁴² The first need is a sorbent with a suitable adsorption capacity under ultradilute conditions. As noted above, we have introduced supported amine materials as effective materials for this application. However, while sorption capacity is the easiest metric to target and assess in a scientific study (hence its overemphasis in the scientific community), 26 it must be coupled with good sorption kinetics, which is the second need. Large capacity with rapid sorption/desorption kinetics is a key practical need. However, these parameters are intimately linked with the sorption process design, and often cannot be fully inferred from the lab scale fixed bed or TGA experiments that are most often utilized. This leads to the third key need, a sorption process that allows for ultralow pressure drops. Because CO₂ is so dilute in ambient air, a very large volume of gas must be moved through a DAC process compared to traditional postcombustion CO₂ capture processes. As such, a process that achieves very low pressure drops is acutely needed. The lowest achievable pressure drops in gassolid contacting are generally achieved using monolith contactors such as those ubiquitously used in automotive catalytic converters. To this end, we have promoted their use, along with Global Thermostat LLC, as a key component of a practical DAC process. In much the same way that catalytic materials are coated on the walls of monolith contactors for exhaust gas cleanup, supported amine sorbents, or other sorbent materials, can also be incorporated into monolith contactors. This yields a gas-solid contacting strategy that can in principle couple very low pressure drops (on the order of hundreds of Pa at linear gas velocities of 2-5 m/s), rapid sorption/desorption kinetics, and good CO₂ capacities.

The fourth key need for a practical DAC process is a low cost mode of sorbent regeneration. In the cyclic sorption/ desorption process, sorption is exothermic and occurs spontaneously. Thus, aside from the cost of moving the air through the process, there are no significant energy inputs. In contrast, the desorption process is endothermic, and energy must be added to the process to desorb and concentrate the CO₂. CO₂ capture using supported amine sorbents is most often achieved using a temperature swing (TSA) for desorption, though there are distinct advantages to the possible combination of temperature and vacuum for desorption (TVSA).^{34,43} A key advantage of supported amine adsorbents is that they are low temperature chemisorbents that sorb CO₂ under ambient conditions and thus require only a temperature rise from ambient to 70-120 °C (or less if vacuum is applied) for desorption. In this temperature range, there is ubiquitous waste heat available around the globe that could be used to generate steam for desorption. In the case of a monolith contactor, the direct flow of low temperature saturated steam can induce desorption by condensation on the sorbent surface by providing both a thermal and concentration driving force for desorption. This steam/sorbent contacting leads directly to the fifth need for a practical DAC process, sorbents that have high stability under the process conditions utilized. In this regard, for supported amine sorbents in DAC, two modes of sorbent degradation have been evaluated in detail by our group.⁴

The first sorbent degradation mode is oxidation. Unlike flue gas, which contains typically <5% O₂, air contains substantial

oxygen (21%). The combination of elevated temperature and high oxygen concentrations can lead to significant amine degradation via irreversible oxidation. Fortunately, we,⁴⁵ in parallel with independent studies by the groups of Calleja⁴⁶ and Sayari,⁴⁷ demonstrated that primary amines are quite stable to oxidation under the expected conditions encountered in CO₂ capture processes. In contrast, secondary amines can oxidize easily to imines and amides, reducing their basicity, under some conditions relevant to DAC. The observation that the most important amines for CO₂ capture under ultradilute conditions, primary amines,⁴⁰ are also the most stable to oxidation, was a fortunate finding.

Given that primary amines were shown to be the most useful under ultradilute conditions for CO₂ capture and that they were more stable than secondary amines, a potential replacement for the most commonly used polymer, PEI, was sought. Highly branched PEI is a highly effective CO₂ sorbent, due to its large density of primary amine at chain ends displayed toward the outside of the polymer, with less useful secondary and tertiary amines buried in the interior. However, the secondary amines still play an important role in CO₂ capture, and their loss due to oxidation quite often impacts the function of adjacent primary amines.⁴⁵ To this end, we demonstrated the utility of the linear, primary amine rich polymer, poly(allylamine) (PAA), as a possible surrogate for PEL.³² While PEI proved to be marginally more effective than the first generation, linear PAA polymer at similar amine loadings in capturing CO₂, the potential for producing an oxidatively stable PAA polymer that rivals the performance of PEI is high, with minor tuning of the polymer structure.

The second mode of sorbent deactivation that our group explored was degradation due to steam exposure. Because silica is solubilized under basic conditions, we hypothesized that traditional aminosilica composite materials would not be stable under steaming conditions, and for this reason we have also focused on the use of alumina supports. Indeed, our initial investigations of highly porous silicas functionalized with amines under steaming conditions demonstrated that their porosity was lost under mild steaming conditions.^{48,49} In contrast, the use of alumina supports imparted improved steam stability,^{31,50} while yielding effective CO₂ sorbents when expensive, micelle-templated alumina was used as the support.⁵¹ Expensive organic-templated supports are not practical for use in this application at large scales, and typical commercially available aluminas have lower porosity than commercial silicas, such that there is a potential trade-off between support porosity and amine loading (silica better) with steam stability (alumina better).

Of the five needs associated with a practical process for DAC—(i) sorption capacity, (ii) sorption kinetics, (iii) low pressure drop, (iv) practical sorbent regeneration, and (v) long sorbent lifetime—the first four needs have been demonstrated in our work, on a first-principles basis. Although the peer reviewed literature is dominated with studies focusing on the first need, the use of monolith contactors has the potential to offer outstanding performance with regard to the second and third needs.⁵² Sorbent regeneration using steam-stripping with direct sorbent contacting has also been demonstrated using both silica and alumina based amine sorbents.^{50,53} The biggest remaining unknowns regarding the practicality of DAC using amine sorbents revolve around the fifth need. While extensive sorbent stability studies have been conducted by us as well as others (vide supra), only long-term testing in the field can give

the data needed to truly assess the potential of amine sorbents for use in practical air capture processes.

SUMMARY AND CONCLUSIONS

Building on an infrastructure developed for the creation of welldefined amine-functionalized silica surfaces for applications in catalysis, an initial collaboration with researchers at NETL effected a new emphasis on the use of amine-oxide hybrid materials for CO_2 capture from flue gases. This collaboration led to the development of new materials for CO_2 capture, referred to as hyperbranched aminosilica materials, prepared by the in situ polymerization of aziridine or azetidine in and on a porous oxide support.

A collaboration with Global Thermostat LLC catalyzed the exploration of supported amine materials of all types for direct air capture. We have demonstrated that supported amine materials of all types—class 1, class 2, and class 3—were effective at extraction of CO_2 from simulated ambient air, and that they can be regenerated under mild conditions such as steam-stripping. The importance of the amine type on the efficacy of capture, the adsorption thermodynamics, and the sorbent stability have been studied in detail. Primary amines have been demonstrated to be the most effective under air capture conditions as well as the most stable toward degradation via oxidation.

We have outlined the major technical requirements of a practical air capture process, and accumulated data suggesting that supported amine materials when combined with monolith contactors can, in principle, offer a platform from which extraction of CO_2 from ambient air might be feasible on a large scale. However, significant unknowns still remain, chiefly centered around the long-term stability of the sorbents under extended, practical operating conditions, as well as the long-term operation of the hypothesized TSA or TVSA process based on the amine sorbent/monolith contactor combination. It is in these areas that future research should be focused so as to continue pushing this technology forward.

In parallel, just as our work on carbon capture grew out of previous work on aminosilica materials used in catalysis, the materials developed here for CO_2 capture have now been used in other applications as well, including the capture of ultradilute VOCs from ambient air,^{54,55} as well as in selective hydrogenation catalysis.⁵⁶ The materials have clearly motivated others to develop related porous materials for CO_2 capture using amine-modified porous polymers^{57–59} and MOFs,^{60–64} signaling that hybrid amine materials have much to offer for a variety of applications in catalysis and separations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.ac-counts.5b00284.

Discussion of merits of DAC as a carbon mitigation technology (PDF)

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Accounts of Chemical Research

Author Contributions

The manuscript was written through contributions of all authors, but was primarily written by C.W.J.

Notes

The authors declare the following competing financial interests: C.W.J. has a financial interest in Global Thermostat Operations, LLC. Global Thermostat Operations, LLC, is an affiliated company to Global Thermostat, LLC, who funded part of this work. C.W.J. has a conflict-of-interest control plan in place at Georgia Tech, which requires (amongst other things) that the statement of financial interest, made above, appears in papers where the research was funded in whole or in part by Global Thermostat LLC.

Biographies

Stephanie A. Didas is from the Bay Area of California. She received her B.S. degree in chemical engineering in 2009 from UC Berkeley. Following this, she moved to Atlanta, GA to study chemical engineering at Georgia Tech under the supervision of Prof. Christopher W. Jones. She received her M.S. and Ph.D. degrees in 2014 for work related to the design and characterization of amineoxide materials for CO_2 capture from air. She currently is the Managing Director of UNCAGE-ME, an Energy Frontier Research Center at Georgia Tech, as well as the Group Manager for Prof. Christopher Jones' research group.

Sunho Choi was born in Seoul, Korea and received his B.S. degree in 2000 with a First Class Honor in Materials Science from Hanyang University. After 3 years at Samsung Electronics, he moved to the University of Minnesota in 2003 for his Ph.D., where he worked with Prof. Michael Tsapatsis while studying zeolitic layered materials synthesis and membrane separations. In 2008, he moved to Georgia Tech as a Camille and Henry Dreyfus Foundation Postdoctoral Fellow in Environmental Chemistry, where he worked with Prof. Christopher Jones for inorganic–organic hybrid adsorbents for CO_2 capture. In 2011, he moved to Northeastern University as an assistant professor of Chemical Engineering. His current research program focuses on porous nanomaterials and their hybrids for advanced separation and catalysis.

Watcharop Chaikittisilp was born and raised in Bangkok, Thailand. He obtained his BEng degree with a First Class Honors and Gold Medal in 2003 from Chulalongkorn University (Thailand). Thereafter, he received a Monbukagakusho scholarship from MEXT and joined The University of Tokyo (Japan) where he obtained MEng (2006) and Ph.D. (2010) degrees in Chemical System Engineering under the supervision of Prof. Tatsuya Okubo. After working as a postdoctoral fellow with Prof. Christopher W. Jones at the Georgia Institute of Technology, and subsequently as a MANA research associate at the National Institute for Materials Science (Japan), he moved back to The University of Tokyo, where he is now an assistant professor. His current research interests include designed synthesis of zeolites and nanoporous organic–inorganic hybrid materials, and their applications toward sustainability.

Christopher W. Jones was raised in Troy, MI, before attending the University of Michigan, where he obtained a BSE degree in chemical engineering in 1995. He subsequently moved to Pasadena, CA, to attend Caltech and work with Prof. Mark E. Davis, where he obtained M.S. and Ph.D. degrees in chemical engineering in 1997 and 1999, respectively, while studying zeolite synthesis and catalysis. Following a 1 year postdoctoral period in chemistry at Caltech working with Davis and Prof. John E. Bercaw, whereby he studied supported olefin polymerization catalysts, Jones moved to Georgia Tech, where today

he is the New-Vision Professor of Chemical & Biomolecular Engineering and Associate Vice President for Research. His research program focuses on materials for catalysis and separations, leveraging synthetic chemistry to solve engineering challenges.

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ABBREVIATIONS

HAS, hyperbranched aminosilica; PEI, poly(ethylenimine); DAC, direct air capture; PAA, poly(allylamine); DOE, Department of Energy; NETL, National Energy Technology Laboratory

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