

## Solid Sorbents Report

When a gas makes contact with a solid, it can be taken up by the solid, just as gaseous odors in your refrigerator can be taken up by activated charcoal or baking soda. The gas either enters the solid (absorption) or remains adhering to the surface of the solid (adsorption). The processes of adsorption and absorption by a solid are collectively referred to as sorption. The solid which takes up the gas is the adsorbent, and the gas adhering to the surface is called the adsorbate. It is not easy to distinguish whether the gas is adsorbed or absorbed because most solid materials have pores into which gases can diffuse, and there is not a common technique that could be used to distinguish the two processes if they are occurring simultaneously. However, it should be noted that since adsorption requires a gas molecule to make stronger contact to a surface than to itself, the process of adsorption brings gas molecules closer to each other on the surface than without the surface. The gas molecules make contact with the surface through *physisorption* (weakly bound to the surface through polarizing forces) or *chemisorption* (strongly bound to the surface through strong covalent bonds). This sorption is more energetically favorable than compacting gases by application of high pressure or low temperature.

Sorbent materials have a number of design criteria. First, it preferable to design surfaces that minimizes the energy required to remove the adsorbed gas from the surface (i.e., physisorption requires lower energy to release the gas than chemisorptions). The increased energy required to release the gas can contribute substantially to the cost of electricity, for example. Second, the gas capture material should have high capacity, meaning that it should possess a large number of surface adsorption sites to which gases may bind. Thus the design of materials with high surface areas is important. High surface area may be achieved either by making small particles of adsorbents or making materials with highly porous internal structures. Examples of such porous solids include zeolites, and activated carbon (see Sidebar A), which have surface areas ranging

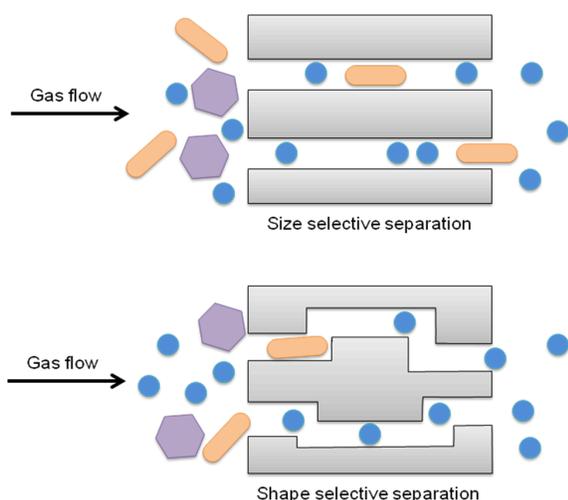


Figure 1. Selectivity of adsorbent is can be designed into the material

A third key requirement for solid sorbents is to design the material to allow selectively remove a target gas molecule from mixtures. This selectivity allows the pores to be filled preferentially one gas relatively pure gas, which subsequently released, allowing the porous material to be reused. The selective binding of a specific gas molecule is done in a porous material by matching the pore openings with the shape and size of that gas molecule (shape- and size-selective binding, as shown in **Figure 1**).

Additionally, it is possible to also design the steric, electronic, and chemical properties of the adsorption sites within the pores to make the material more highly selective to specific gas molecules.

The discussions below focus on development of revolutionary new materials are of interest for post-combustion processing of gas streams such as those found in pulverized coal power plants as well as those applicable in pre-combustion IGCC systems and that might allow oxygen separation and transport to enable oxy-combustion systems. These materials will be critical for establishing future technologies for minimizing CO<sub>2</sub> emissions into the atmosphere when fossil fuels or biomass is combusted to produce energy.

**Post Combustion:** In post combustion whether the system is a conventional coal plant or natural gas turbines of combusting biomass, the challenge is to separate a dilute stream of CO<sub>2</sub> from a atmospheric pressure flue gas at less than 200 °C that contains ~78-80% N<sub>2</sub>, 2-6% O<sub>2</sub>, H<sub>2</sub>O and 10-14% CO<sub>2</sub>, depending on whether it is from coal fired plants, oil burners or natural gas turbine. Thus post combustion technologies must take separate CO<sub>2</sub> at modest concentration and at modest pressures. Under these conditions solid sorbents could offer significant advantages over conventional amine-based liquid stripping techniques if the net energy for uptake and release can be optimized and the materials are sufficiently stable upon cycling<sup>i ii</sup> One twist on the amine-based stripping is to graft the amine functionalities onto the solids which avoids the energy penalty for heating water but it would still involve breaking covalent bonds between CO<sub>2</sub> and the amine functionality.<sup>iii iv</sup> However, these materials face challenges with chemical stability and maintaining the mechanical stability of solid amine pellets as the system is cycled.

An attractive alternative for solid adsorbents include classes of materials that have three-dimensional architectures [see sidebar B] that increase the surface area available for sorption and thereby increase the capacity of the material. To ensure facile kinetics for uptake and release of CO<sub>2</sub> solid sorbents can be designed to have very large surface-to-volume ratios with the majority of materials comprised of porous solids or high surface area particulates, such as activated carbon<sup>v</sup>, zeolites and other porous silica-based materials.<sup>vi</sup> The primary mode of CO<sub>2</sub> uptake is physisorption, resulting from interactions between the gas and the material. The current limitations of these types of solid adsorbents for gas sorption include low capacity of CO<sub>2</sub> uptake in porous carbons and the energy required for removal of CO<sub>2</sub> from zeolites.

There is enormous potential for making these solid materials highly selective for the adsorption of targeted gases by modifying the surface of these materials.<sup>vii</sup> For example, activated carbon materials can be enriched with elements that could give improved properties. These include substitution of some carbon atoms by nitrogen or impregnating the material with metal ions. These ‘extraframework’ atoms and metals ions can serve as specific site for selective adsorption of CO<sub>2</sub>.<sup>viii</sup> When the interior pores of activated carbons zeolites or mesoporous silicates are functionalized with amines they can reversibly form surface-tethered carbamates upon exposure to induce chemisorption and increasing the uptake efficiency at low partial pressures of<sup>ix, x xi, xii</sup>. A similar surface functionalization approach can be applied to the surface of small particles providing a high surface area solid support amine functionalization. While these initial studies show considerable promise a molecular understanding of the interaction of targeted gases with these functionalized is critically needed. This understanding will catalyze the design of new,

more selective sorbents. This knowledge will also help explain the role of moisture content on the uptake and release efficiency as these new materials are used in real applications.<sup>xiii</sup> One could ask if extensions of to active materials that can respond to magnetic fields to facilitate concentration of the CO<sub>2</sub> carriers or couple to RF radiation to transducer energy for release are possible in carrier particles. Incorporating a supporting particle that exhibits a phase transformation near the temperature of separation could allow the exothermic energy of CO<sub>2</sub> uptake to be adsorbed and later recovered to aid in CO<sub>2</sub> release.

A new class of materials that have considerable potential as solid sorbents include metal-organic frameworks (MOFs) and zeolitic imidazolate frameworks (ZIFs) [sidebar B]. These novel crystals and network solids combine well-defined coordination environments surrounding metal centers with bridging organic ligands. The wide range of metals and ligands that can be incorporated in these structures can yield an enormous variety of porous structures.<sup>xiv</sup> The MOFs and ZIFs can separate targeted gases by physisorption or by chemisorptions. For example, in a MOF it is possible to bind CO<sub>2</sub> in one of at least three ways which provide progressively stronger binding energy and therefore more heat is needed to remove the CO<sub>2</sub>: (1) physisorption onto the vast internal surface, (2) adsorption onto open metal sites within the backbone of MOF structure where CO<sub>2</sub> binds directly to the metal sites through the carbon atom, and (3) by functionalizing the organic links with amine functionality and binding CO<sub>2</sub> in a chemisorption fashion. .... with the associated formation of carbamates when the organic linker expresses free amine functionality.<sup>xv xvi</sup> As with the earlier mesoporous approaches the MOFs and ZIFs the energy penalty of the sensible heat of the aqueous amine stripping solutions but incur losses for the temperature swing release cycle. Some members of the MOFs and ZIF families show sufficient thermal and structural stability for extended cycling. MOFs and ZIFs are to some extent all surface area with pore reach to molecular dimensions. In these systems one can ask if CO<sub>2</sub> binding can be coupled to a collective exothermic physical distortion of the MOF or ZIF bonding network that could provide for energy recovery in the CO<sub>2</sub> release cycle. Here, the use of a flexible MOF whose structure expands and contracts upon carbon dioxide binding and release, may provide a net exothermic process which reduces the energy required to release the CO<sub>2</sub> by heating alone. Because of the large number of possible compositions and structures there is considerable research potential in the exploration of MOF and ZIF structures and in their evaluations with respect to CO<sub>2</sub> uptake and release.

**Pre-combustion:** In a pre-combustion process, as in an IGCC system, fuel is reacted with oxygen and/or a mixture of steam and air to produce a hot stream of CO, H<sub>2</sub> and H<sub>2</sub>O can provide power in a coupled steam cycle and then passed over a water gas shift catalyst to convert CO and H<sub>2</sub>O to a stream rich in CO<sub>2</sub> and H<sub>2</sub>. The H<sub>2</sub> can, in turn, be combusted in a gas turbine with further greenhouse emissions or in the future might be coupled with a hydrogen fuel cell to allow more thermodynamically efficient conversion.<sup>xvii</sup> In pre-combustion systems, CO<sub>2</sub> is present in high concentration and at high temperature in precombustion power systems where CO<sub>2</sub> separation during combustion can improve combustion efficiency while further CO<sub>2</sub> subsequent stage of with water gas shift catalysis can significantly increase the efficiency of conversion and production of H<sub>2</sub>. There may be opportunities for some applications of mesoporous solids, or MOFs and ZIFs but the low energy of binding and limited temperature stability of these systems will be a challenge. Under these pre-combustion conditions reversible

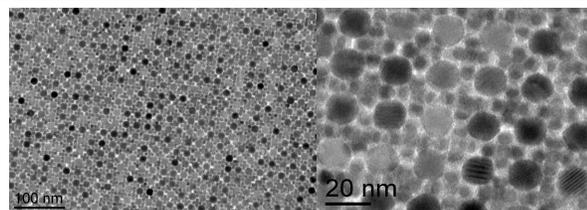
formation of inorganic carbonates is a more promising area for exploration. In this case  $\text{CO}_2$  is reacted with abundant earthen oxides such as calcium oxide, to produce stable carbonates.<sup>xviii</sup>,<sup>xix</sup> The reaction in nature is slow and can take many years but it can be made faster by increasing the temperature and by maximizing the available surface area of the particles.<sup>xx</sup>,<sup>xxi</sup> In certain circumstances the Ca based sorbents can serve to remove both  $\text{SO}_2$  as well as  $\text{CO}_2$  simplify reactor design and separate acid gas scrubbing.<sup>xxii</sup> Spraying water based slurries of  $\text{NaHCO}_3$ , or  $\text{Na}_2\text{CO}_3$  in to a hot  $\text{CO}_2$  rich flow can allow the formation of particulate carbonates that can be recovered and reprocessed<sup>xxiii</sup>. Optimization of particle composition size and structure offer potential for further improvements but new compositions are showing new options.

Although the thermochemical behaviour of zirconates was studied much earlier<sup>xxiv</sup> the relevance of these systems for high temperature  $\text{CO}_2$  capture was only recently appreciated<sup>xxv</sup> Lithium zirconate  $\text{Li}_2\text{ZrO}_3$  is a particularly promising candidate for  $\text{CO}_2$  separation at the high temperatures experienced in a pre-combustion style reactor.<sup>xxvi</sup> <sup>xxvii</sup> Although it has been shown that pure  $\text{Li}_2\text{ZrO}_3$  absorbs a large quantity of  $\text{CO}_2$  at high temperatures with a relatively slow sorption rate the “addition of potassium carbonate ( $\text{K}_2\text{CO}_3$ ) and  $\text{Li}_2\text{CO}_3$  in the  $\text{Li}_2\text{ZrO}_3$  remarkably improves the  $\text{CO}_2$  sorption rate of the  $\text{Li}_2\text{ZrO}_3$  materials”.<sup>xxviii</sup> In addition to the compositional tuning and exploration of additives the strategy of grain size engineering appears to provide significant benefits. Nanocrystalline zirconates offer markedly enhanced kinetics<sup>xxix</sup> and point to improvements in total capacity with increase surface adsorption.

### Solid sorbents in service of oxy-combustion

**Chemical Looping:** The reversible uptake and release of oxygen by metal and metal oxide particulates offers an innovative approach to combustion of fossil fuels in with a nitrogen free  $\text{O}_2$  ambient thus affording the primary benefit of oxy-combustion, the elimination of the energetically expensive separations of  $\text{CO}_2$  for  $\text{N}_2$  in the flue gas stream.<sup>xxx</sup> It is particularly notable that the initial investigation of chemical looping were undertaken due to its fundamental potential to improve combustion efficiency.<sup>xxxi</sup> If the benefits of simplified  $\text{CO}_2$  capture and separation could be coupled with improved combustion efficiency this could be transformative.

**Oxygen carrier development:** RedOx active transition metal pairs based on Cu, Ni, Fe, Mn and Co have attracted the greatest interest with specific pairs



Model nanoporous oxygen carriers: Advances in nanoscale materials processing may provide important new opportunities to design materials compositional and grain size for CLC applications. Fig (2) above displays a model oxygen carrier assembled from 2 complimentary sizes of iron oxide particles in that can cycle reversibly between the  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ . On the left is the result of the reducing cycle which the panel on the right has been oxidized on exposure to air. This sample was prepared with a predominantly  $\text{Fe}_2\text{O}_3$  stoichiometry and was reduced at 500 C in an anaerobic environment while in contact with oleic acid. The organic is consumed leaving and all inorganic nanoporous network of  $\text{Fe}_3\text{O}_4$ , exposure to Air at ~300C rapidly affects recovery of the  $\text{Fe}_2\text{O}_3$  exploration of with nanoscale. Although the monodisperse 7nm and 15nm grains in the model system greatly aid imaging and modeling of process control of particle size in real world application is likely to be needed only to the extent that it allows optimization of surface area and the interconnected nature of the internal grain boundaries and pores to maximize the rate of oxygen uptake and release. An area of potential interest in new oxygen carrier design is the greater compliance of nanoscale grain that may aid in oxygen uptake/release and facilitate ionic transport in the body of the grains. I like this and the use of materials at the nanoscale should be highlighted in this report

including  $\text{Cu}_2\text{O}/\text{Cu}$ ,  $\text{CuO}/\text{Cu}$ ,  $\text{NiO}/\text{Ni}$ ,  $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ ,  $\text{Mn}_3\text{O}_4/\text{MnO}$ ,  $\text{CoO}/\text{Co}$ .<sup>xxxii</sup>, <sup>xxxiii</sup> The reactive particles are generally formulated with an inert matrix or binder. Binders enhance physical stability of the particle during cycling and reduce the deleterious effects of agglomeration and sintering that could cause coarsening of the active oxygen carrier that could reduce surface area and accessibility significantly reducing reaction kinetics in uptake and release of oxygen. Binders include, metal oxides such as  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{NiAl}_2\text{O}_4$ ,  $\text{CoAl}_2\text{O}_4$ , benonite, Kaolin,  $\text{Ni}_{1-y}\text{Mg}_y\text{Al}_2\text{O}_4$ ,  $\text{ZrO}_2$ , Ytria stabilized Zirconia (YSZ)  $\text{MgO}$  etc. Designing an oxygen carrier with high capacity and facile kinetics dictates solid with exhibits high surface to volume ratio but has a low dead-volume and a pore of grain structure that will facilitate ionic and molecular transport.<sup>xxxiv</sup> The large accessible surface area must be preserved upon many RedOx cycles and at extremely high temperatures ( $>1000\text{C}$ ). A further challenge is the large volume change that can occur in some oxygen carriers upon cycle between their oxidized and reduced states. Engineering compact solids that resist mechanical degradation, in this are the judicious choice of binders is particularly critical. Existing systems have oxygen carriers and binders, have significant potential for further advancement and ref () provides a recent review.

Solid sorbents have huge potential for selective uptake and release of targeted gases in schemes that would be designed to eliminate  $\text{CO}_2$  emissions to the atmosphere that would be incorporated into a process either before or after combustion. Key issues that need to be addressed are:

- 1) Discovery of revolutionary materials with novel architectures and functionalities
- 2) New Triggers for Selective Capture and Release**
- 3) Cooperative Phenomena for low net enthalpy of cycling**

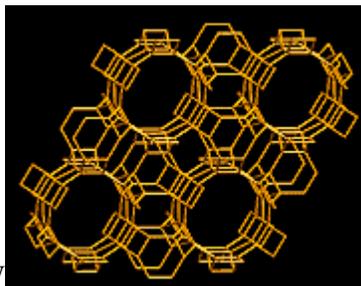
We know little about designing complexity in a controlled fashion on the atomic and nanoscales, and our knowledge is rudimentary of carbon dioxide chemistry and what makes a material a good carbon capture material. Herein, we provide some directions as a sampling of what we believe should be among the many approaches which we should be investigating to overcome the carbon capture challenge.

**Side bar: Zeolites and activated carbon**

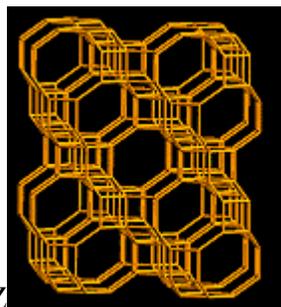
Solid sorbents are commonly found in nature and have been used by man for years to purify gases and liquids. Activated carbon, also called activated charcoal, is a form of carbon that has been processed to make it extremely porous, yielding a very large surface area available for adsorption. Activated carbon is widely used to purify gases, remove impurities from drinking water, filter impurities from aquarium systems, and even absorb poisons from digestive systems in medical applications. Zeolites are also found in nature and are crystalline aluminosilicates with porous structures. Synthetic versions of these materials have been made with oxide structures containing elements other than aluminum and silicon; however all zeolites have well-defined pore structures. The metal atoms in zeolites are surrounded by four oxygens in a tetrahedron geometry. The crystalline materials stack into regular arrays, forming channels that permit gas permeation. Depending upon the atoms and structures used in these materials, the size and shapes of these channels can be tuned to specific dimensions and permit selective passage of different gases, like a virtual “molecular sieve.” To date, thousands of zeolites have been reported based on hundreds of structures. Three types of structures are shown below that illustrate the channels that can form in these materials. Ref: IZA Structure Commission <http://www.iza-structure.org/>



ABW



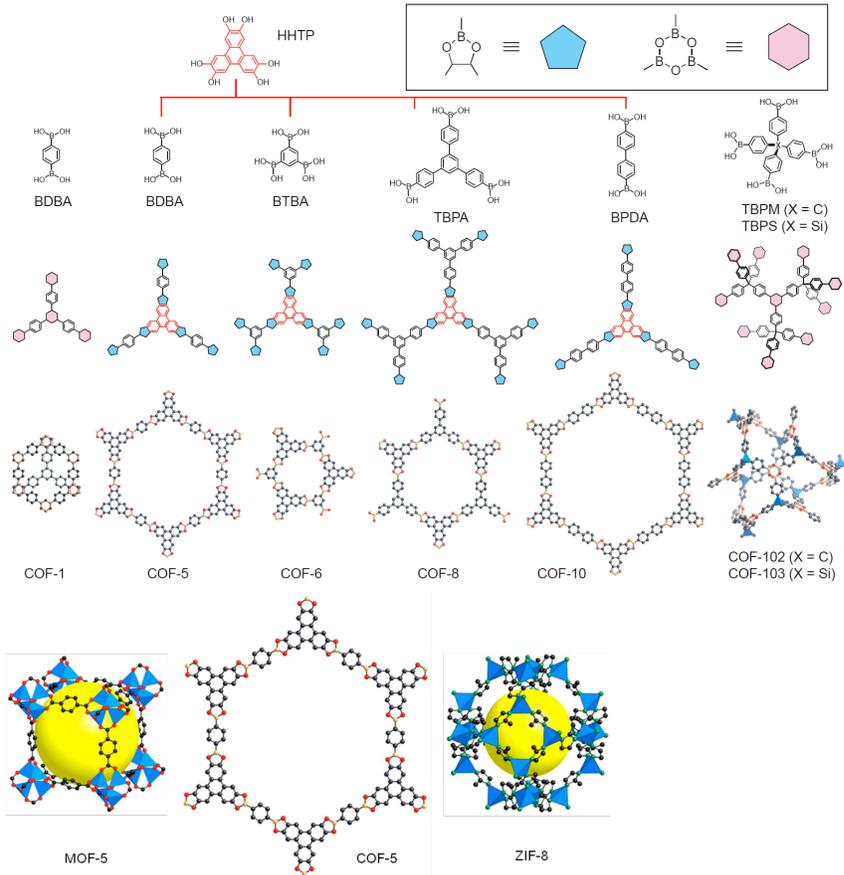
MAZ



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## Sidebar B

### Porous Chemical Architectures



Traditional porous structures are broadly classified in three types: (1) Zeolites, crystalline aluminosilicates and silicate structures that are generally constructed from silicon/aluminum oxide cages which are linked together into extended porous structures. The interior of the cages is inaccessible to gases because of the small window opening, but the extended porous structures they form have large enough channels where gases can be adsorbed. (2) Silicas, mesoporous solids which have ordered pores but amorphous pore walls, and aerogels which have disordered pores and pore-walls. These have had limited application in gas separations because of their disordered structures which lead to lack of specificity in binding gases. (3) Porous carbon, this is of many different kinds; all prepared from carbonaceous starting materials. Porous carbon is difficult to study because of its highly irregular structure. Generally, it has not been as useful as zeolites or other porous materials in gas separations. However, it is useful in water purification and, when impregnated with metals, it could be useful as a support for catalysis. Recently, new classes of molecularly designed crystalline porous solids have emerged as favorable candidates for gas separation and storage. These are metal-organic frameworks

## **PRD 1: Design of Revolutionary materials with novel architectures and functionality**

The ideal solid sorbent material would have designed structures with functionalities optimized for efficient, selective uptake of the targeted gas and facile, low energy release so the sorbent can be cycled an infinite number of times. For example, new sorbent materials can be imagined that incorporate multiple properties, with nanoscale pores altered with specific functional groups that allow them to selectively bind carbon dioxide from combustion gas mixtures and whose release is triggered by a stimulus such as electrical, thermal, chemical or mechanical.

To realize breakthroughs in sorbent materials required for large scale carbon capture schemes, a number of key scientific questions need to be addressed:

1. Can the unprecedented control over structure and properties that has been provided by recent advances in nanoscience be harnessed to enable design and synthesis of new sorbent materials structures tailored for optimum performance?
2. Can surface functionalities, active sites and catalysts be designed and incorporated into sorbent materials to enhance targeted gas sorption while maintaining cyclability?
3. How does a targeted gas interact with a specific site on a sorbent surface—including open sites found on nanoparticles and nanoscale and larger pores in three dimensional structures?
4. Can new classes of sorbents be designed to achieve energy densities far greater than currently available?

**A. Development of methods for producing hetero-constructs in which several materials are juxtaposed and matched synergistically, or mixed at the molecular level to create multivariate functions.** These materials of various functionalities can be formed through unique synthetic techniques ranging at the atomistic level to physically admixing various components. Functional domains with catalytic ability of different heat of adsorption with me incorporated on the molecular or nanoscale level. The potential approaches will require the development of new synthesis techniques/routes, allowing the deposition of a continuous, thin and conformal coating onto high specific surface area substrates.

**B. Develop synthetic methods to produce tunable porous and nonporous materials of localized dynamics within rigid structures.** The sorbents should be strong and durable to withstand multiple (tens of thousands or more) operation cycles. At the same time, switchable or flexible internal structure should be able to accommodate of large amounts of CO<sub>2</sub> without a drastic changing in the macroscopic size/shape, which usually leads to material degradation. For example, there is a rich opportunity to explore designer structures whose porosity might equal or exceed that of currently known porous materials.

**C. Creating material with controllable texture and curvature that allows fine-tuning of binding energy and release rates.** Hierarchical synthesis methodologies based on self-assembly are needed to generate capture sites and ultimately integrated sorption media. Nature has provided an ample number of examples of hierarchal materials that possess precision molecular recognition. The key synthesis strategy underlying the manufacturing

of active sites in nature is the “key-and-lock” principle of templating synthesis and compartmentalization. We anticipate the use of 0-, 1-, 2-, and 3-D nanostructures for carbon dioxide storage.

## **PRD 2: New Triggers for Selective Capture and Release**

A chemical medium (liquid, solid, membrane, etc.) is required for binding and separating CO<sub>2</sub> from other process gases. This step is generally requires energy-intensive swings in temperature and/or pressure to release material after capture. Indeed, nearly 35% of the energy produced in power generation is consumed in these capture-release mechanisms. New approaches that use ‘smart’ materials that respond to alternative energy triggers are needed to overcome the excessive energy costs of the current temperature and pressure approaches.

Such smart materials could be triggered to bind / release targeted gases by alterations of any number of physical or chemical properties that result in a sufficient change in the binding affinity or capacity for carbon dioxide. For example, an electrical potential could be used to increase the binding affinity of select polarizable gases over other gases present in the process stream. Alternatively, this stimulus could be used to cause a conformation change (e.g. alignment of surface functional groups) resulting in a change in binding affinity. In this context, the discovery of new types of conducting porous materials would be of high value. Similarly, the piezoelectric behavior of materials could be used to mechanically/electrically induce structural changes in a solid sorbent that would modulate binding affinity. Irradiation of a carbon dioxide capture material using electromagnetic radiation may induce a resonance phenomena associated with the material, and thus change the nature of carbon dioxide binding. Alternatively, **It may be possible to alter the binding affinity of a material** by application of an external magnetic field. Finally, the selectivity and capacity of capturing a targeted could be designed to be when accompanied by a phase change of the sorbent material.

Designing such smart materials to respond to alternative triggers will require the development of new materials with specific architectures and functionalities that are tailored to respond to the alternative triggers. Computational methods will be invaluable for the design of these smart materials to expedite the optimum structures and functionalities for these new solid sorbents.

The use of triggered smart materials is also not limited to solid adsorbents, but as described elsewhere in this report, is applicable to liquid- and membrane-based strategies as well.

Key questions to be addressed include:

### PRD 3: Cooperative Phenomena for low net enthalpy of cycling

Coupling of gas sorption with the underlying molecular structure of a material may enhance the thermal efficiency. This approach capitalizes on having the sorption/desorption cycle accompanied by a chemical or structure change in a manner akin to ‘cooperative’ phenomena. Here, the fact that the thermodynamics of binding is driven by entropy with minimum *net* enthalpy provides for the needed thermal efficiency. The types of changes that might occur within the materials’ structure span a wide range of length scales, from the molecular to the macroscopic.

Successful integration of this strategy into carbon dioxide capture technology requires not only that net energy expense be low, but also that the rates of uptake and release be high. Since the compensatory coupled materials changes will necessarily be energetically “uphill”, the rates of gas uptake or release could be substantially reduced.

- There are at least four general approaches to the discovery and exploitation of such cooperativity that can be distinguished based on the length-scale of the cooperative interaction: (a) atomically local, (b) molecularly local, (c) nanoscopically and microscopically confined, and (d) macroscopic: ***Atomically local. It is generally the rule, in molecular inorganic chemistry*** for different ligands to affect one another’s binding mode and binding energy. This represents the delicate tailoring of the intimate electronic and structural properties of the very local binding sites.
- *Molecularly local.* There are examples in nature in which the binding of one molecule to an active site in a material increases *its affinity for* binding of a second molecule. Perhaps the most well-known example is that of hemoglobin in which the absorption of one molecule of O<sub>2</sub> to the erstwhile completely deoxygenated substrate affects the thermodynamics and kinetics of the subsequent oxygen coordination steps.
- *Confinement at the molecular level.* Three-dimensional environments can be designed and prepared that behave like “sponges” for the target molecule.
- *Bulk effects.* Phase changes are the quintessential examples of cooperative phenomena. In the present context, the freezing and thawing of CO<sub>2</sub>-saturated water illustrate the accelerative impact that bulk phase changes can have on the absorption of gases. The scientific challenge here is to synthesize materials that can exist in two (or more) phases that have dramatically different CO<sub>2</sub> capacities. The additional critical feature is that the CO<sub>2</sub> be vigorously absorbed or expelled when the material is coaxed from one phase to another by an external stimulus—such as heating, pressure variation (perhaps sonically), application of a voltage or magnetic field, or through irradiation with light.

**A. Investigation of the rates of gas uptake and release in cooperative systems.** The kinetics for reversible gas sorption in these cooperative systems is as important as the low overall energy budget. Interfaces—between gases and solids and between different solids—are gating factors in determining the rate for any gas sorption process. Changes induced by binding of molecular gases can occur on different length scales, from the molecular to the macroscopic. Materials transformations are known to be triggered by external stimuli. For example, piezoelectric materials—materials in which mechanical deformations produce electrical fields and vice versa—expand or contract.

**B. Discovery and elucidation of new structure-function relationships in complex materials.** Research should provide for a thorough understanding of the structures and related energetics of the starting and resulting materials. This will be especially important for materials involved in carbon dioxide binding and transport. Emphasis should be on elucidation of new compositionally-driven structural changes. Concomitant with any structural or chemical change is a change in the underlying electronic structure. Together, these create the energy landscape for a chemical transformation.

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