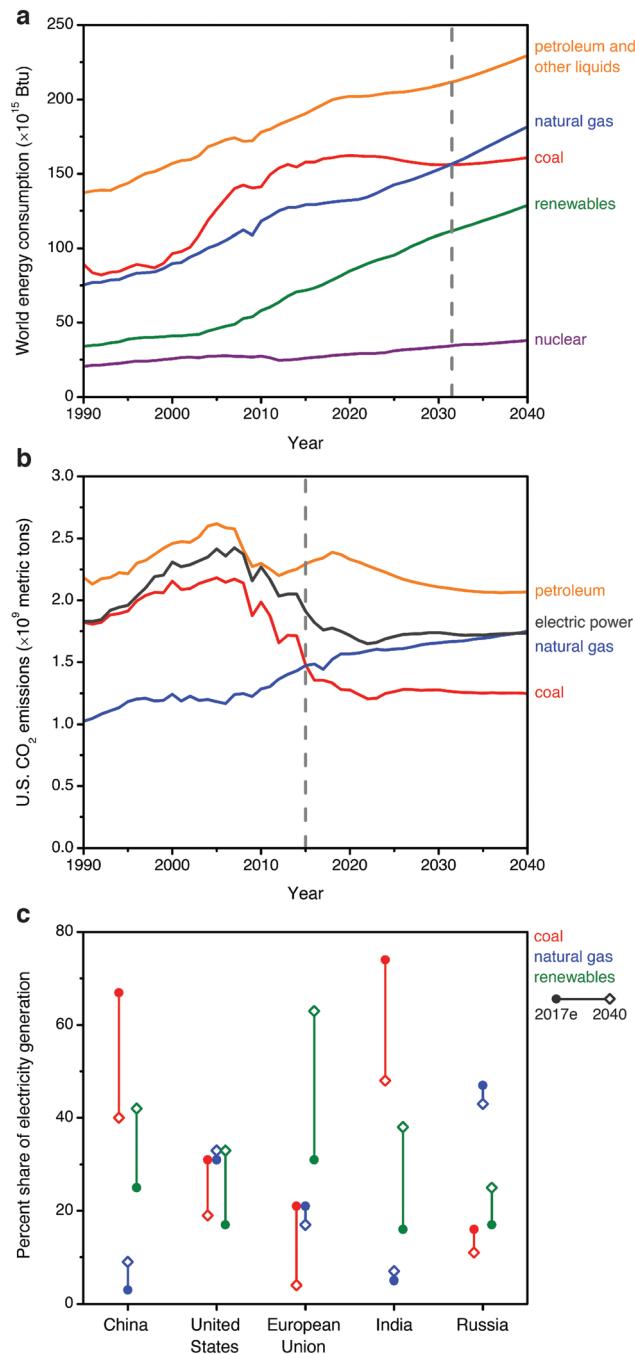




To date, the vast majority of CCS studies have focused on coal-fired power plants,<sup>7,9</sup> as the combustion of coal is currently responsible for approximately 27% of the global energy supply and 44% of anthropogenic energy-related CO<sub>2</sub> emissions.<sup>2,6,7</sup> However, natural gas is the fastest-growing fossil fuel source in terms of worldwide consumption (increasing with a compound average annual growth rate of ~1.9% per year, compared to ~0.1% per year for coal), and it is projected to overtake coal in terms of contribution to global energy by 2030 (2018 New Policy Scenario, International Energy Agency)<sup>10</sup> or 2032 (U.S. Energy Information Administration, Fig. 1a).<sup>11</sup> Although global gas-related emissions are not predicted to surpass those from the combustion of coal until after 2040,<sup>10</sup> this transition has already occurred in select important regional markets where natural gas is already a major fuel source for energy production, such as the United States (Fig. 1b), the United Kingdom, and Russia.<sup>2,12,13</sup>

The growing worldwide consumption of natural gas is due to increasingly available reserves and its low greenhouse gas footprint relative to coal, since the combustion of natural gas produces approximately half as much CO<sub>2</sub> as the combustion of coal per kW h of energy produced.<sup>14</sup> Indeed, recent declining emissions in the electric power sector for natural gas-dominant regions such as the United States correlate closely with a shift in the energy landscape from coal to renewable sources and natural gas (Fig. 1b), although overall CO<sub>2</sub> emissions remain substantial.<sup>12</sup> Considering the role of natural gas in electric power generation for other major energy stakeholders, forecasts remain highly sensitive to region-specific policy, market, and technology factors. In Fig. 1c, we show the current and projected fuel distribution<sup>10</sup> for regions responsible for the largest portions of global CO<sub>2</sub> emissions from fuel combustion: China (28.0% of global CO<sub>2</sub> emissions), the United States (15.0%), the European Union (9.9%), India (6.4%), and Russia (4.5%).<sup>2</sup> In 2040, natural gas will likely continue to constitute a major portion of electricity generation in the United States and Russia, the largest current markets. In China and India, coal will likely continue to supply a major fraction of electric power in the near-term, but modest increases are anticipated in the share of gas-fired electricity generation in these countries.<sup>10</sup> In the European Union, the overall use of fossil fuels for electric power continues to decline, but coal use is projected to decay at an accelerated rate compared to natural gas use.<sup>10</sup> In light of these trends, near- and long-term research is urgently needed to address the unique challenges of CCS from natural gas-fired power plants, in conjunction with ongoing efforts toward CCS from coal-fired power plants.<sup>6,7,13,15,16</sup>

The conditions for carbon capture from natural gas and coal flue gases are relatively similar, with several key differences. Both flue gas streams are released at atmospheric pressure, are generated at high temperatures (> 80 °C) but typically cooled to 40–60 °C to enable effective CO<sub>2</sub> capture, and consist primarily of CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub>.<sup>6,13,17,18</sup> However, while coal flue gas streams typically contain relatively high CO<sub>2</sub> concentrations (~15%), the typical flue gas from a natural gas combined cycle (NGCC) power plant contains 3.9% CO<sub>2</sub> with a balance of 74.4% N<sub>2</sub>, 12.4% O<sub>2</sub>, 8.4% H<sub>2</sub>O, and 0.9% Ar,<sup>18</sup> rendering CO<sub>2</sub> capture



**Fig. 1** (a) Historical and projected worldwide consumption of energy sources from 1990–2040, suggesting that consumption of natural gas will match that of coal by ~2032 (dashed gray line).<sup>11</sup> (b) Historical and projected CO<sub>2</sub> emissions from the combustion of fossil fuels and the overall electric power sector from 1990–2040 in the United States, a representative natural gas-centric energy economy. Natural gas overtook coal in contributing to anthropogenic U.S. CO<sub>2</sub> emissions after 2015 (dashed gray line).<sup>12</sup> (c) Estimated current (2017e) and projected 2040 shares of electricity generation (percent of TW h) by fuel for selected regions, following the 2018 New Policy Scenario of the International Energy Agency.<sup>10</sup>

from NGCC flue emissions more technically challenging.<sup>13,14,16,17,19</sup> (Simple-cycle power plants with gas-fired boilers, which emit flue

gas streams containing higher CO<sub>2</sub> concentrations of 7–8% but operate with lower efficiencies,<sup>8</sup> are not addressed in this perspective.) A second challenge is the much higher concentration of O<sub>2</sub> in NGCC flue gas (12.4%) compared to that in coal flue gas (~4%).<sup>13,16</sup> However, natural gas flue emissions contain a much lower concentration of other corrosive components, such as SO<sub>x</sub>, and other contaminants, such as NO<sub>x</sub>, heavy metals, and particulate matter, resulting in an overall cleaner stream than coal flue gas.<sup>18</sup> Thus, effective materials for CO<sub>2</sub> capture from NGCC power plants must be thermally and oxidatively stable while demonstrating strong, selective adsorption of CO<sub>2</sub> at low concentrations ( $\leq 3.9\%$ ) under humid conditions, but their stability to SO<sub>x</sub> and NO<sub>x</sub>, a limiting challenge for CO<sub>2</sub> capture from coal-fired power plants, is less critical.

Many of the design principles developed for coal flue gas capture should translate to the development of new materials for capture from natural gas flue emissions.<sup>7,13,14,16</sup> Designing efficient capture systems is critical, because up to 80% of the cost of CCS from a natural gas-fired power plant accrues during the CO<sub>2</sub> capture step.<sup>20</sup> The most technology-ready materials for CCS are aqueous amine solutions, due to their low cost and selective reaction with CO<sub>2</sub>.<sup>21,22</sup> Indeed, a pilot-scale demonstration (1991–2005) of CO<sub>2</sub> capture from the Bellingham NGCC power plant in the United States employed the Econamine FG PlusSM amine-based technology, and the use of several other advanced amine scrubbers has been demonstrated at the Test Centre Mongstad facility in Norway.<sup>13</sup> Despite their advanced state of development, aqueous amine solutions continue to suffer from a number of drawbacks, including low working capacities (<2 wt%), high regeneration temperatures (>120 °C), and oxidative and thermal degradation during long-term cycling.<sup>23–28</sup> These challenges are exacerbated in a natural gas post-combustion capture process, where the high regeneration temperatures required to desorb strongly-bound CO<sub>2</sub> and the high O<sub>2</sub> content of the target stream lead to increased thermal and oxidative amine degradation (discussed further below).<sup>13,16</sup>

Due to these drawbacks, significant research efforts have been directed toward the development of new strategies to reduce CO<sub>2</sub> emissions from fossil fuel-fired power plants. Several engineering solutions have been explored to integrate CO<sub>2</sub> capture with plant operation, including the use of molten carbonate fuel cells for simultaneous concentration of CO<sub>2</sub> (up to ~75%) and excess power production,<sup>29</sup> as well as the Allam cycle, in which CO<sub>2</sub> is used as the working fluid in an oxy-fuel process to yield high-pressure, pipeline-quality CO<sub>2</sub>.<sup>30,31</sup> In addition, new materials have been designed for post-combustion CO<sub>2</sub> capture,<sup>6,7,32,33</sup> including water-lean liquid absorbents<sup>34,35</sup> and membranes.<sup>7,36</sup>

Recently, porous solids such as zeolites, carbons, silicas, porous polymers, and metal-organic frameworks have also been studied extensively for carbon capture applications, due to their potential to achieve larger CO<sub>2</sub> working capacities and improved cycling stabilities compared to aqueous amine solutions.<sup>7,37–65</sup> However, nearly all studies to date have focused on CO<sub>2</sub> scrubbing from coal flue gas, direct capture from air, and removing CO<sub>2</sub> from crude natural gas, with very few studies investigating adsorptive capture from natural gas flue emissions.<sup>13,16,66</sup>

Therefore, this perspective focuses on the unique challenges and opportunities inherent to the application of adsorbents for CCS from NGCC power plants, which remains an underdeveloped but important area of research. Specifically, we will examine (i) the challenges unique to adsorptive CO<sub>2</sub> capture from natural gas flue emissions, (ii) promising materials for this process that warrant further study, and (iii) recommended experiments to assess the suitability of new carbon capture materials.

## Challenges associated with capture from natural gas flue emissions

### Low partial pressure of CO<sub>2</sub>

The low concentration of CO<sub>2</sub> in natural gas flue emissions is due to the large excess of air that is used as a thermal diluent during combustion (200–250% of the stoichiometric O<sub>2</sub> requirement).<sup>19</sup> This low concentration (3.9%) renders CO<sub>2</sub> capture from natural gas flue gas more energetically demanding than from coal flue gas.<sup>13,16–19,51,67</sup> Therefore, adsorbents for the target process must possess high adsorption capacities (ideally  $>2\text{--}3\text{ mmol g}^{-1}$ ) at low CO<sub>2</sub> concentrations ( $\leq 3.9\%$ ) with adsorption temperatures of  $\geq 40\text{ }^{\circ}\text{C}$ .<sup>44,68,69</sup> In order to achieve the U.S. Department of Energy's target of 90% CO<sub>2</sub> capture from the flue gas stream,<sup>18</sup> materials would need to demonstrate adsorption at CO<sub>2</sub> concentrations as low as 0.39%. Many adsorbents explored to date for CCS from coal-fired power plants are unable to adsorb appreciable quantities of CO<sub>2</sub> at such dilute levels. Furthermore, such strong adsorption typically necessitates large CO<sub>2</sub> adsorption enthalpies,<sup>70</sup> which in turn can lead to large temperature increases in the adsorbent bed—and significant losses in CO<sub>2</sub> working capacity—if the heat release is not properly managed.<sup>71</sup> An additional consequence of this requirement is a high theoretical minimum work for a CCS process (0.14–0.20 MJ per kg CO<sub>2</sub>),<sup>7</sup> leading to high regeneration temperatures and energies in a temperature swing adsorption (TSA) process or very low desorption pressures in a vacuum swing adsorption (VSA) process.<sup>44</sup>

Despite the higher theoretical minimum work for CO<sub>2</sub> capture from NGCC power plants, CCS from gas-fired plants may be less costly than from coal plants when considering the levelized cost of electricity (LCOE), the average lifetime unit cost of electricity generation of a power plant.<sup>72,73</sup> Recent estimates suggest that the LCOE for NGCC power plants would increase from 42–83 USD per MW h without CCS to 63–122 USD per MW h with CCS, while that of supercritical pulverized coal-fired plants would increase from 61–79 USD per MW h without CCS to 95–150 USD per MW h with CCS (costs are in constant 2013 USD and include capture, transport, and geological storage).<sup>73</sup> The potentially lower LCOE for NGCC power plants with CCS is favored in the case of low gas prices and reflects the lower emission intensity of natural gas, because a post-combustion capture system at a NGCC plant would process only approximately half as much CO<sub>2</sub> as a capture system at a coal plant.<sup>8,72,73</sup> However, specific cost estimates should be

interpreted with caution, due to the large number of region-dependent technical, economic, and financial assumptions required, as well as remaining uncertainty resulting from a lack of empirical data from full-scale demonstrations.<sup>74</sup> As capture systems progress toward full-scale deployment, continued refinement of techno-economic models will help narrow the wide range of projected costs for specific projects. In addition, advanced capture technologies may enable more favorable techno-economic analyses, but additional data and larger-scale demonstrations are needed to reduce the even greater degree of uncertainty for cost predictions with these systems.

Recently, engineering strategies have been developed to increase the partial pressure of CO<sub>2</sub> in NGCC flue gas and thus allow for more efficient CO<sub>2</sub> capture. One such strategy is exhaust gas recycling, in which recycled flue gas (~4% CO<sub>2</sub>, ~12% O<sub>2</sub>) is used in place of air (400 ppm CO<sub>2</sub>, ~21% O<sub>2</sub>) during the fuel combustion process (Fig. 2).<sup>15,17,67,75–77</sup> This strategy produces flue gases with enriched CO<sub>2</sub> concentrations of up to ~8%, making CO<sub>2</sub> capture less thermodynamically challenging.<sup>17</sup> Indeed, recent techno-economic analyses have suggested that coupling up to 50% flue gas recycling with the use of aqueous monoethanolamine (MEA) for CO<sub>2</sub> capture should lead to a lower energy penalty on a natural gas-fired power plant than the use of aqueous MEA alone.<sup>15,17,67,78,79</sup> However, the use of >35% exhaust gas recycling requires significant capital investment with respect to the combustion unit and is unlikely to be a retrofit option for current power plants, and therefore an optimal balance exists between the extent of exhaust gas recycling and the energy penalty of the carbon capture step.<sup>17</sup> In a related strategy under development, membranes can be used to recycle CO<sub>2</sub> selectively from flue gas to the combustor, increasing the concentration of CO<sub>2</sub> in the final flue gas stream up to ~19% with almost no thermodynamic penalty.<sup>19</sup> Although the use of membranes for pre-concentrating CO<sub>2</sub> would lead to increased capital and maintenance costs, the benefit of the subsequently more favorable CO<sub>2</sub> capture step may ultimately make this strategy more feasible. Overall, the use of flue gas recycling or membrane pre-concentration strategies simplifies the carbon capture step but requires additional capital costs compared to a direct capture configuration, which mandates significant techno-economic analysis to determine the ideal CCS strategy for a given power plant.

## High partial pressure of O<sub>2</sub>

The large excess of air used as a thermal diluent during the combustion of natural gas also contributes to a high O<sub>2</sub> content (12.4%) in the flue gas stream,<sup>18,19</sup> which can accelerate the oxidative degradation of aqueous amine solutions.<sup>13,16</sup> Although the mechanisms by which aqueous amines degrade in the presence of O<sub>2</sub> have been well studied,<sup>25,26,80</sup> significantly less attention has been paid to the oxidative stability of porous solids for CO<sub>2</sub> capture, such as metal-organic frameworks and porous organic networks.<sup>81</sup> Overcoming this barrier will be a primary challenge in the commercialization of CO<sub>2</sub> capture adsorbents specific to NGCC flue gas, and further discussion of oxidative stability is included in subsequent evaluation of individual adsorbent classes. For amine-functionalized adsorbents, recent studies have demonstrated that materials functionalized with secondary amines, such as polyethylenimine, are subject to CO<sub>2</sub> capacity loss upon extended exposure to O<sub>2</sub>, but materials functionalized with primary amines possess significantly improved oxidative stability.<sup>27,81–86</sup> Spectroscopic studies have suggested that the main oxidation products of amine-functionalized materials are imines and carbonyl-containing species such as amides, imides, and carboxylic acids.<sup>82,87–89</sup>

One potential engineering solution to the oxidative degradation of carbon capture materials is flue gas recycling, which has the added benefit of depleting the O<sub>2</sub> content of the flue gas stream (down to ~4% O<sub>2</sub> with 50% recycling), in addition to increasing the CO<sub>2</sub> content.<sup>17</sup> When exhaust gas recycling is combined with stoichiometric combustion, excess O<sub>2</sub> may be essentially eliminated from the flue gas, and CO<sub>2</sub> exhaust concentrations as high as approximately 20% can be achieved.<sup>90</sup> Nonetheless, the current lack of information on the oxidative stability of porous materials hinders further development of adsorbents for CO<sub>2</sub> capture from NGCC flue emissions. Beyond oxidative stability, the CO<sub>2</sub>/O<sub>2</sub> selectivity and resulting influence on the purity of captured CO<sub>2</sub> will also need to be assessed.

## Saturation with water

A critical challenge shared by adsorption-based CO<sub>2</sub> capture from coal and natural gas flue gas is that both streams are saturated in H<sub>2</sub>O (up to 10% by volume), which mandates that a prospective material not only capture CO<sub>2</sub> selectively in the

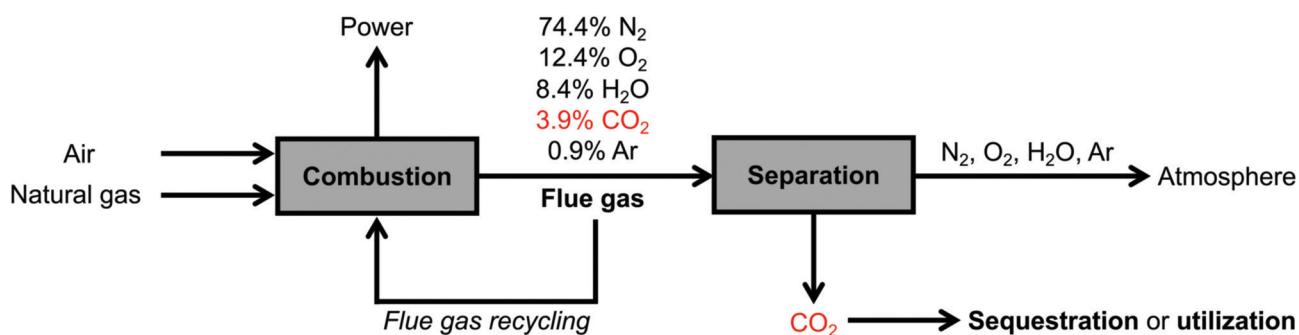


Fig. 2 Schematic of a natural gas-fired power plant with post-combustion CO<sub>2</sub> capture, including optional flue gas recycling to increase the concentration of CO<sub>2</sub> in the flue gas up to ~8%.

presence of  $\text{H}_2\text{O}$ , but also possess long-term stability under humid conditions.<sup>18,39,44,46,48</sup> Furthermore, parasitic energy costs associated with cycling of any co-adsorbed water must be minimized.<sup>69</sup> Challenges related to water saturation are particularly onerous for  $\text{CO}_2$  removal from NGCC flue gas, which contains more than twice as much water (8.4%) as  $\text{CO}_2$  (3.9%), in contrast to coal flue gas, which contains nearly twice as much  $\text{CO}_2$  as water.<sup>18</sup> Although the flue gas stream can be dried prior to  $\text{CO}_2$  removal, a dehydration unit would likely be extremely costly and impractical on large scale.<sup>91</sup> The presence of water in the flue gas stream is problematic for materials relying on equilibrium selectivity for  $\text{CO}_2$  at exposed metal ions, such as certain zeolites and metal-organic frameworks, as these sites have been shown to adsorb water preferentially over  $\text{CO}_2$  in both multicomponent measurements and theoretical calculations.<sup>46,92–100</sup> In contrast, amine-functionalized materials often show improved  $\text{CO}_2$  adsorption capacities under humid conditions.<sup>41,92,101,102</sup> Amine-functionalized adsorbents may also benefit from humidity through the mitigation of deleterious urea formation.<sup>41,103,104</sup> Nonetheless, a dearth of information persists for a range of promising materials regarding competitive  $\text{CO}_2$  adsorption under humid conditions and the costs associated with the desorption of co-adsorbed water.<sup>92,105</sup> Overall, the requirement for selective adsorption of  $\text{CO}_2$  in the presence of water is often the primary barrier that precludes the application of a new adsorbent for  $\text{CO}_2$  removal from flue gas.

## Key opportunities and promising adsorbents for capture from natural gas flue emissions

Despite the above-mentioned challenges, gas-fired power plants offer a number of advantages over coal plants in post-combustion capture processes beyond the overall reduction in  $\text{CO}_2$  emissions before capture. First, the combustion of natural gas typically generates significantly fewer contaminants. While coal can contain high levels of mercury (up to 0.15 ppm, dry weight) and sulfur (up to ~3 wt%), gas-fired plants generate no mercury waste and emit only trace amounts of  $\text{SO}_x$ .<sup>18</sup> Furthermore, the generation of particulate matter is significantly reduced for NGCC plants compared to coal plants.<sup>18</sup> This cleaner emission stream relaxes the need for adsorbents that are stable to trace  $\text{SO}_x$  or for extensive pre-treatment to protect the  $\text{CO}_2$  adsorbent. Considering the experimentally-observed poisoning of a wide array of adsorbents by  $\text{SO}_x$  and  $\text{NO}_x$ ,<sup>85,106–112</sup> CCS efforts on cleaner NGCC flue gas streams may lead to extended adsorbent lifetimes and thereby increase the techno-economic favorability of adsorptive  $\text{CO}_2$  capture. Second, the installation of innovative capture technology may be more straightforward at gas plants than at coal plants, where the  $\text{CO}_2$  capture system must be integrated with upstream pollutant control systems.<sup>13</sup> Finally, while the cost of capture is typically higher for natural gas plants due to the more dilute stream, lifecycle analyses have suggested that the cost of integrating CCS into a new natural gas plant may approach that of a retrofit capture system at an aging coal plant.<sup>113</sup>

Targeted exploration of adsorbents for carbon capture from natural gas power stations has been relatively limited to date, with the majority of post-combustion capture studies instead focused on coal flue emissions. Although adsorbents capable of direct capture of  $\text{CO}_2$  from air<sup>59</sup> may prove effective for capture from NGCC flue gas, these materials will likely require excessively high regeneration energies due to the stronger binding enthalpies typically needed to capture  $\text{CO}_2$  at ppm levels. Therefore, adsorbents previously investigated for  $\text{CO}_2$  capture from coal flue gas and air provide a basis for our discussion of promising candidate materials for CCS from natural gas flue emissions, but further research is required to design materials and capture systems specifically for this challenging capture process. In general, the most promising adsorbents share a common feature of strong binding sites, such as amines, that enable selective adsorption of  $\text{CO}_2$  at low partial pressures from humid flue gas (Fig. 3).

### Zeolites

Zeolites are crystalline, microporous aluminosilicates that can be extracted as minerals or produced synthetically. These materials have already achieved commercialization in industrial gas separations, and a wealth of knowledge is available regarding their incorporation into engineered forms within full-scale processes.<sup>114</sup> For carbon capture applications, the mechanism of separation typically relies upon preferential interaction of the quadrupole moment of  $\text{CO}_2$  with the electric field of cations within the zeolite pores, enabling strong  $\text{CO}_2$  binding at low partial pressures.<sup>115,116</sup> The crystalline nature of these materials and the comprehensive library of known and predicted structures make zeolites particularly well-suited for computational evaluation; indeed, previous studies have leveraged these properties to predict the optimal zeolites for  $\text{CO}_2$  capture from both coal<sup>117</sup> and natural gas<sup>51</sup> flue emissions.

Initial studies of zeolites specific to  $\text{CO}_2$  capture from NGCC flue gas included an evaluation of zeolite 13X in an electric swing adsorption (ESA) process, where an electrical regeneration energy of 2.04 GJ per ton  $\text{CO}_2$  was reported, excluding compression energy and water removal.<sup>118</sup> However, zeolites such as 13X that operate *via* equilibrium adsorption mechanisms suffer from a critical limitation: water typically outcompetes  $\text{CO}_2$  at cationic binding sites, leading to loss of selectivity for  $\text{CO}_2$  in humid flue gases.<sup>92,119,120</sup> Future research in zeolite-based processes for  $\text{CO}_2$  capture from natural gas flue emissions must take this limitation into account by designing innovative materials or processes to overcome water passivation or by incorporating increased capital and operating costs to pre-dry the flue gas stream.<sup>91</sup>

Despite these limitations, zeolites remain attractive candidates for separations under harsh conditions due to their high thermal, oxidative, and hydrolytic stability. This stability arises from the strong tetrahedral Al–O and Si–O bonds of the inorganic backbone, as well as the relatively small increase in energy for permanently porous phases compared to analogous condensed structures.<sup>121</sup> Moving forward, amine-functionalized zeolites (Fig. 3a) merit further study for  $\text{CO}_2$  capture from natural gas flue emissions due to their strong  $\text{CO}_2$  binding at low partial

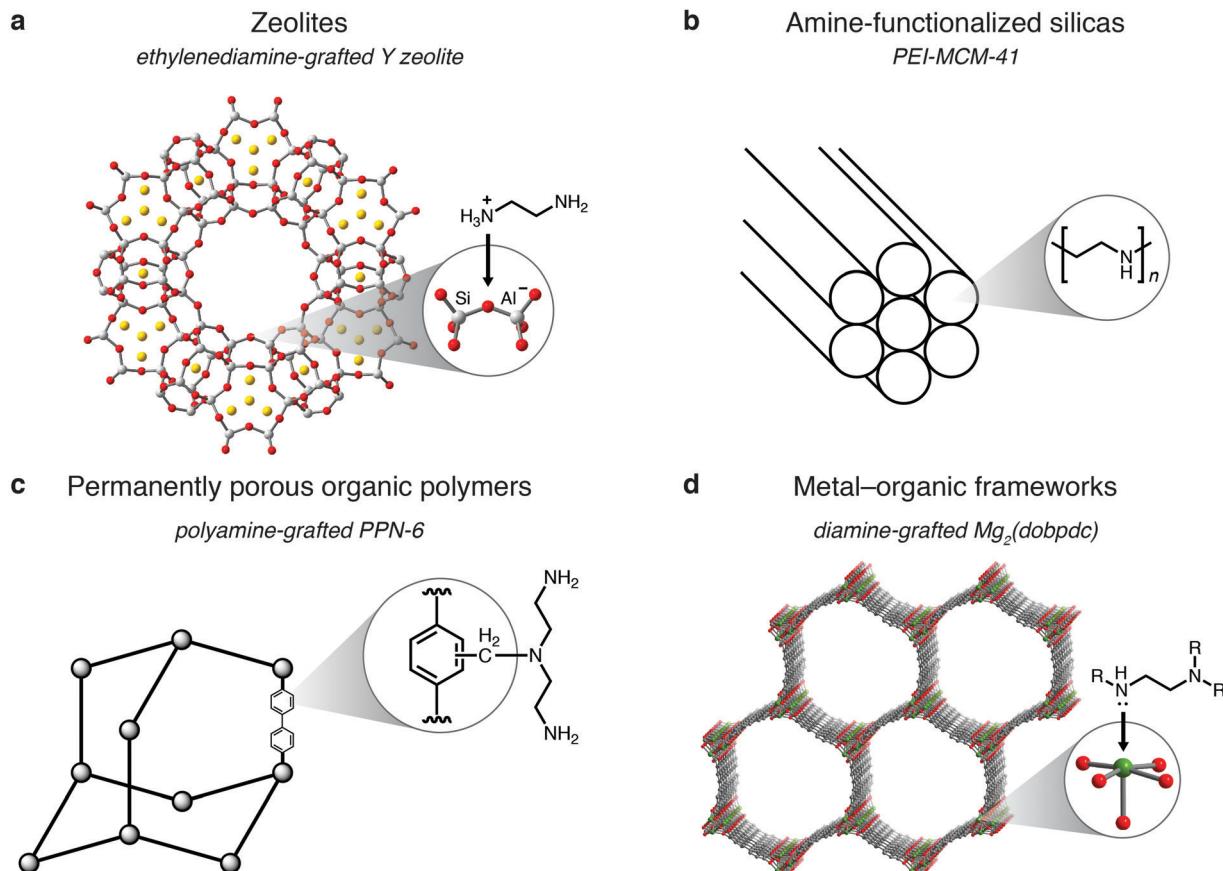


Fig. 3 Promising adsorbents for post-combustion capture from NGCC flue gas require strong and selective binding sites, such as amines, to enable  $\text{CO}_2$  adsorption at low partial pressures under humid conditions. Promising material classes and specific examples include (a) zeolites, such as an ethylenediamine-grafted Y zeolite<sup>93</sup> (silver, red, and yellow spheres represent Al/Si, O, and Na atoms, respectively); (b) amine-functionalized silicas, such as PEI-MCM-41<sup>101</sup> (PEI = polyethylenimine); (c) permanently porous organic polymers, such as polyamine-grafted PPN-6;<sup>137,138</sup> and (d) metal–organic frameworks, such as diamine-functionalized variants of  $\text{Mg}_2(\text{dobpdc})$ <sup>148</sup> (green, red, and grey spheres represent Mg, O, and C atoms, respectively; H atoms are omitted for clarity).

pressures and their selectivity for  $\text{CO}_2$  in the presence of water.<sup>93,122–125</sup> However, incorporation of amines may result in lower stability for the resulting organic–inorganic hybrid materials. For example, composite materials formed by physical impregnation of zeolite NaX with MEA or tetraethylenepentamine (TEPA) were found to undergo significant amine volatilization upon 24 h of exposure to flowing  $\text{N}_2$  at 130 °C, a realistic desorption temperature for TSA cycling with NGCC flue gas.<sup>93</sup> As a notable improvement, a recently reported ethylenediamine-Y zeolite bearing chemically grafted amines was shown to possess thermal stability up to 180 °C.<sup>93</sup> Chemical grafting of amines to the zeolite scaffold was also found to suppress urea formation as compared to a PEI-impregnated silica (PEI = polyethylenimine), a result the authors attributed to strongly co-adsorbed water within the hydrophilic zeolite pores.<sup>93</sup> Critically, the oxidative stability of these organic–inorganic hybrid materials and their resulting suitability for  $\text{CO}_2$  capture from NGCC emissions remain untested.

#### Amine-functionalized silicas

The impregnation (Class I) or covalent grafting (Class II) of (poly) amines within porous silicas has been demonstrated as a strategy

to generate highly selective  $\text{CO}_2$  capture adsorbents.<sup>41,64,126,127</sup> These materials typically bind  $\text{CO}_2$  by chemisorption to form ammonium carbamate and/or carbamic acid species depending on the identity and proximity of amine functionalities.<sup>128</sup> Importantly, chemisorption of  $\text{CO}_2$  enables many amine-functionalized silicas to preserve selectivity for  $\text{CO}_2$  in the presence of water, typically with improved capacities, due to the formation of bicarbonate species.<sup>41,101</sup>

Despite the dearth of information specific to NGCC post-combustion  $\text{CO}_2$  capture for other adsorbent classes, a few reports have already discussed the application of amine-functionalized silicas for this separation. In breakthrough experiments with simulated flue gas containing 7.4–7.7%  $\text{CO}_2$ , 14.6%  $\text{H}_2\text{O}$ , and ~4.45%  $\text{O}_2$  (similar to what would be expected for a simple-cycle gas-fired process or an NGCC process with flue gas recycling), PEI-MCM-41 (Fig. 3b) was shown to capture  $\text{CO}_2$  selectively in two consecutive adsorption/desorption cycles.<sup>129</sup> A techno-economic study benchmarking this material against a conventional MEA solvent process (following the U.S. Department of Energy's NGCC base case<sup>18</sup>) indicated a potential 21% reduction in capital costs as well as a lower cost of electricity

and cost of CO<sub>2</sub> avoided compared to the MEA process.<sup>130</sup> More recently, a combined experimental and theoretical study of a PEI-functionalized silica reported a regeneration heat of 5.0 GJ per ton CO<sub>2</sub> captured for a NGCC plant (compared to 4.2 GJ per ton for a pulverized coal plant).<sup>69</sup> In a sensitivity analysis, this study suggested that development of optimized adsorbents with large CO<sub>2</sub> capacities (>4 mmol g<sup>-1</sup>) could dramatically reduce the regeneration heat, as would the use of a direct contact cooler to limit the water content of the flue gas.<sup>69</sup> Another process simulation study with a PEI-functionalized silica adsorbent likewise found that the net plant efficiency could be increased with enhanced CO<sub>2</sub> working capacities and reduced water co-adsorption, and that improved heat recovery and the use of steam for desorption could lead to further gains in efficiency.<sup>131</sup>

Despite these promising initial studies, key challenges remain for this class of materials, including amine oxidation, urea formation, leaching of amines from Class I materials, and slow adsorption/desorption kinetics in certain diffusion-limited variants.<sup>37,41</sup> Recent work has demonstrated that the incorporation of longer alkyl spacers between amines,<sup>132</sup> integration of hydrogen bonding groups,<sup>89</sup> and addition of small amounts of chelators to remove oxidation-catalyzing trace metal impurities<sup>133</sup> can dramatically improve the oxidative stability of these materials. These recent findings merit further study toward the application of amine-functionalized silicas for CO<sub>2</sub> capture from natural gas flue emissions.

### Porous organic networks

Permanently porous purely organic materials can be prepared *via* crosslinking of multitopic organic monomers to achieve amorphous porous organic polymers or crystalline covalent-organic frameworks. These materials offer a number of advantages in carbon capture processes, including modular pore size and surface functionality, high stability, and the potential for high gravimetric capacities through the use of light elements in the polymer backbone.<sup>134–136</sup> However, experimental evaluation of porous organic polymers specific to post-combustion capture from NGCC power stations has been extremely limited to date. A computational study of CO<sub>2</sub> capture from dry NGCC flue gas with several materials, including zeolites, metal–organic frameworks, porous organic polymers, and hypothetical adsorbents, found a group of amine-functionalized porous polymer networks (PPNs) to be the most promising candidates for this separation.<sup>51</sup> These materials feature a biphenyl-based, diamond-like polymeric support (PPN-6, also known as PAF-1) that is post-synthetically covalently functionalized with polyamines, enabling strong and selective CO<sub>2</sub> binding at low partial pressures (Fig. 3c).<sup>137,138</sup> A series of PPN-6 materials functionalized with triethylene-tetramine (TETA), tris(2-aminoethyl)amine (TAEA), and diethylene-triamine (DETA) groups were found to offer parasitic energies of 807, 858, and 880 kJ per kg CO<sub>2</sub>, respectively, with all other examined materials requiring parasitic energies in excess of 900 kJ per kg CO<sub>2</sub>.<sup>51</sup> Importantly, the same computational study identified the DETA-containing derivative as the top-performing adsorbent for direct capture of CO<sub>2</sub> from air (400 ppm CO<sub>2</sub>, 1215 kJ per kg CO<sub>2</sub>) and the TETA-containing derivative as the

second-best candidate for capture from coal flue gas (14% CO<sub>2</sub> in N<sub>2</sub>, 742 kJ per kg CO<sub>2</sub>).<sup>51</sup> These results highlight the overlap in materials effective for each of these separations.

Due to the constituent covalent bonds, many porous organic networks possess significant hydrothermal stability.<sup>139</sup> While the oxidative stability of polymers has been studied more broadly over the past several decades,<sup>140</sup> much remains unknown regarding the stability of porous organic networks in the context of CO<sub>2</sub> capture. To date, exploration of O<sub>2</sub> adsorption by these materials has largely been limited to application in direct air capture (DAC) of CO<sub>2</sub>. Room-temperature O<sub>2</sub> isotherms for a series of amine-functionalized porous polymers showed low O<sub>2</sub> uptake, leading to a high selectivity predicted for CO<sub>2</sub> over N<sub>2</sub> and O<sub>2</sub> on the basis of ideal adsorbed solution theory calculations and transient breakthrough simulations.<sup>138</sup> Nonetheless, further work is needed to probe the oxidative stability of these materials under the gas compositions and higher temperatures relevant to post-combustion CO<sub>2</sub> capture from gas-fired power plants.

Moving forward, materials bearing amine functionalities or other CO<sub>2</sub> chemisorption sites should be a primary focus of porous organic network development for CO<sub>2</sub> capture from low partial pressure streams.<sup>136</sup> Kinetics data, cycling tests, and multicomponent experiments incorporating H<sub>2</sub>O and O<sub>2</sub> are also needed to support further evaluation of porous polymers for post-combustion capture applications. In addition, the ability of these materials to be synthesized at scale and formulated into industrially relevant structured forms remains to be demonstrated.

### Metal–organic frameworks

Metal–organic frameworks consist of inorganic ions or clusters connected by bridging organic ligands, enabling control of pore size, shape, and surface chemistry to target strong and selective binding of specific adsorbates.<sup>141,142</sup> As with zeolites, metal–organic frameworks possess crystalline structures that facilitate precise characterization of framework–guest interactions. The multitude of possible structures accessible with metal–organic frameworks has led to a proliferation of synthetic and computational reports on these materials for carbon capture, with a particular emphasis on post-combustion capture from coal-fired power plants.<sup>42,61,62,143,144</sup>

Many studies have focused on the use of metal–organic frameworks bearing metals with open coordination sites to bind CO<sub>2</sub> selectively over N<sub>2</sub>. However, these binding sites can suffer from the same water passivation issues encountered with cationic binding sites in zeolites.<sup>92,96–98</sup> As an alternative approach, amine-functionalized metal–organic frameworks have been found to combine the advantages of crystalline materials with the selective reactivity toward CO<sub>2</sub> demonstrated by amine-grafted silicas, amine-functionalized porous polymers, and amine solutions.<sup>145,146</sup> Amine functionalities can be incorporated pre- or post-synthetically within the organic bridging ligands or post-synthetically onto open metal coordination sites within the framework. The latter strategy recently led to the development of adsorbents that bind CO<sub>2</sub> cooperatively and reversibly through CO<sub>2</sub> insertion into metal–amine bonds to form ammonium carbamate chains (Fig. 3d).<sup>147</sup> These materials

feature step-shaped  $\text{CO}_2$  adsorption isotherms, and the threshold pressure for cooperative adsorption can be tailored to match the conditions of post-combustion capture from NGCC power stations.<sup>105,148</sup> Certain cooperative, amine-appended frameworks have shown stable temperature-swing cycling performance under humid coal flue gas streams,<sup>105,149</sup> as well as high predicted  $\text{CO}_2/\text{O}_2$  selectivities,<sup>149,150</sup> but more work is needed to assess the thermodynamics and kinetics of  $\text{CO}_2$  capture from streams relevant to NGCC plants, including lower  $\text{CO}_2$  concentrations, higher  $\text{O}_2$  and  $\text{H}_2\text{O}$  concentrations, and higher desorption temperatures. In a related approach, framework surfaces bearing metals bound by a monodentate hydroxide ligand were recently demonstrated to have large  $\text{CO}_2$  capacities under simulated coal flue gas conditions through the reversible formation of metal-bound bicarbonate—a strategy that could also prove effective for capture from natural gas flue emissions, pending further evaluation of the oxidative and hydrothermal stability of these materials.<sup>151</sup>

Despite these promising advances in fundamental materials design, several major challenges remain in advancing metal-organic frameworks toward industrial application. First, as with porous polymers, the majority of frameworks are synthesized as powders, but industrial application will require formulation of shaped particles, monoliths, or fibers. Additionally, limited hydrothermal stability remains a barrier for many frameworks due to the lability of metal-ligand coordination bonds.<sup>152</sup> Oxidative stability is likewise a challenge for many metal-organic frameworks, with oxidation possible at the metal node<sup>153</sup> and/or the organic linker,<sup>154</sup> particularly in the presence of both  $\text{O}_2$  and  $\text{H}_2\text{O}$ .<sup>155–157</sup> Furthermore, development of metal-organic frameworks at a scale relevant to post-combustion capture will require thoughtful selection of earth-abundant metals and inexpensive organic bridging units as well as exploration of alternatives to classic solvothermal synthetic routes, which rely on costly and environmentally harmful organic solvents. Considering the early stage of development of metal-organic frameworks, large-scale demonstrations are needed within relatively short timeframes to encourage continued investment in their commercialization for carbon capture.

## Evaluating adsorbents for capture from natural gas flue emissions

Effective deployment of adsorbents for post-combustion carbon capture at NGCC power plants will require rapid down-selection of the most promising materials for testing at the pilot scale

and beyond. As the number of reported carbon capture adsorbents continues to increase, standardized performance metrics are needed to determine the viability of new capture materials and identify the top performers. Here, we propose a series of experiments to evaluate materials at the laboratory scale (*i.e.*  $< 1\text{ g}$ ). This series of tests will require only a small set of additional experiments for adsorbents already under evaluation for  $\text{CO}_2$  capture from air or coal flue gas. While these suggestions are intended primarily for experimentalists, we stress the critical role that computation can play in evaluating known and possible adsorbent structures.<sup>51,143</sup>

In experimental or computational research, it is important to evaluate adsorbents under realistic conditions, particularly with respect to the high water and  $\text{O}_2$  content in natural gas flue emissions. Practicing scientists and engineers in the carbon capture community have long appreciated these concerns; however, with researchers from more diverse backgrounds continuing to bring valuable expertise to the field, it is important to review these considerations and associated experiments here. We also emphasize that all research on adsorbents for carbon capture would benefit immensely from closer collaboration between materials scientists and process engineers from the earliest stages of development. The ultimate success of adsorption-based processes hinges not only on fundamental material design, but also on the optimization of a structured adsorbent (*e.g.*, pellets, monoliths, or fibers) within a full-scale process.<sup>158,159</sup> To that end, toolsets such as those developed by the Carbon Capture Simulation Initiative (CCSI) will be invaluable in dramatically reducing overall development timelines by optimizing process design concepts and guiding sensitivity analysis within techno-economic models.<sup>160,161</sup>

Specific challenges associated with carbon capture from natural gas flue emissions are summarized and paired with corresponding suggested experiments in Table 1. We discuss each of these approaches in greater detail in the subsequent sections.

### $\text{CO}_2$ adsorption capacity, working capacity, and thermodynamics

To minimize the energy penalty associated with  $\text{CO}_2$  capture from natural gas flue emissions—here taken as a stream of 4%  $\text{CO}_2$  in  $\text{N}_2$  at  $\sim 1$  bar total pressure—adsorption capacities of at least 2–3 mmol  $\text{g}^{-1}$  at 40 mbar of  $\text{CO}_2$  are desirable.<sup>44,68,69</sup> This is because larger  $\text{CO}_2$  adsorption capacities typically correlate with lower energy requirements, particularly for TSA processes.<sup>51</sup> Flue gas typically exits the heat recovery/steam generation unit at 80–120 °C and can be sent to a direct contact cooler to reduce the temperature further to a minimum of

**Table 1** Specific challenges for post-combustion  $\text{CO}_2$  capture from natural gas-fired power plants paired with suggested experiments to probe adsorbent performance

Challenge	Experiment(s)
Low partial pressure of $\text{CO}_2$	Equilibrium studies to probe adsorption capacity for $\text{CO}_2$ under 40 mbar or 4% $\text{CO}_2$ at 40 °C
High partial pressure of $\text{O}_2$	Characterization of oxidative stability under harshest anticipated cycling conditions
Saturation with water	Multicomponent experiments to probe cycling stability and $\text{CO}_2$ capacity under humid simulated flue gas
Selective $\text{CO}_2$ adsorption	Multicomponent experiments to probe selectivity for $\text{CO}_2$ over other contaminants ( $\text{O}_2$ , $\text{N}_2$ )
Slow kinetics	Thermogravimetric analysis, breakthrough, and/or zero-length column experiments with 4% $\text{CO}_2$ in $\text{N}_2$

~40 °C.<sup>79</sup> Because Langmuir-type adsorbents typically show the largest adsorption capacities at the lowest possible adsorption temperature, we suggest that a temperature of 40 °C be used for standardized comparisons of adsorption capacity. However, adsorbents capable of operating with similar or improved performance at higher adsorption temperatures should be highlighted for their potential to decrease cycle times in TSA processes and enhance the overall cycling efficiency. In addition, higher-temperature adsorption data are valuable to inform process models and predict the effect of thermal fronts on the adsorbent efficiency.

The single-component adsorption capacity of a material can be readily extracted from adsorption isobars or isotherms under the appropriate conditions (4% CO<sub>2</sub> at ≥40 °C, or 40 mbar of CO<sub>2</sub> assuming adsorption at 1 bar). Beyond adsorption capacity, projected working capacities are needed to assess the viability of new adsorbents. Many different cycling configurations may be considered, including TSA, pressure or vacuum swing adsorption (PSA or VSA), electrical swing adsorption (ESA), steam stripping, or a combination thereof.<sup>7</sup> Note that desorption with an inert purge gas such as Ar or N<sub>2</sub> is not viable for large-scale application, as this will compromise the CO<sub>2</sub> product purity necessary for subsequent compression, transportation, and sequestration steps.

To design the optimal capture process for a particular adsorbent and calculate the resulting regeneration or parasitic energy, an understanding of the thermodynamics of CO<sub>2</sub> adsorption (and, ideally, of H<sub>2</sub>O, N<sub>2</sub>, and O<sub>2</sub> adsorption) is also needed. For early-stage materials research, knowledge of the adsorption enthalpy of each flue gas component is valuable and can be calculated from the single-component adsorption isotherms. These values are particularly critical for NGCC capture processes, where the large adsorption enthalpies required to capture CO<sub>2</sub> at low partial pressures tend to increase the regeneration energy, as highlighted above.<sup>70</sup> Importantly, the CO<sub>2</sub> adsorption enthalpy is typically already reported for materials designed with direct air capture and/or post-combustion capture from coal flue gas applications in mind, and therefore expanding the application scope of these adsorbents to include capture from natural gas flue emissions should pose no added experimental burden.

### Effect of impurities on CO<sub>2</sub> capacity and selectivity

Competitive models and/or multicomponent measurements are needed to determine the effect of flue gas impurities on the CO<sub>2</sub> capacity and selectivity of an adsorbent. For natural gas flue emissions, the primary contaminants of interest are O<sub>2</sub> and H<sub>2</sub>O, which are both present at higher partial pressures than CO<sub>2</sub>. Therefore, extensive analyses are needed to evaluate the stability and performance of adsorbents under the specific conditions relevant to natural gas flue emissions.<sup>18</sup>

Simple qualitative experiments can enable rapid assessment of the stability of candidate adsorbents to impurities. For example, changes in the single-component CO<sub>2</sub> adsorption capacity after exposure to hot O<sub>2</sub>- and/or H<sub>2</sub>O-containing streams can reveal oxidative or hydrolytic instability in a simulated temperature-swing process. Secondary analysis techniques, such

as infrared spectroscopy, can then be used to probe the mechanism of degradation. Importantly, while adsorbent exposure to individual impurities can help identify specific degradation pathways, the combination of O<sub>2</sub> and H<sub>2</sub>O is known to cause enhanced degradation of many porous materials and should therefore also be considered.<sup>155–157</sup>

Beyond validation of stability, several techniques may be used to probe competitive adsorption. Selectivity can rapidly be calculated from single-component isotherms over a broad parameter space using ideal adsorbed solution theory (IAST), given that the assumptions of the theory hold or that appropriate corrections are applied.<sup>162–164</sup> Experimental characterization under simulated flue gas, while more complex and labor-intensive, is ultimately necessary to evaluate the performance of new materials. When instrumentation permits, multicomponent equilibrium measurements coupled with residual gas analysis are ideal for quantitative characterization of competitive adsorption.<sup>92</sup> Breakthrough experiments with simulated flue gas are likewise informative and more routine, although larger sample sizes (~1 g or greater) are preferable. As an alternative technique, temperature-programmed desorption (TPD) coupled with spectroscopy or mass spectrometry can also be used to quantify co-adsorbed species after exposure to a simulated flue gas stream.

### Long-term cycling stability

Adsorbents for post-combustion capture must be able to withstand extended cycling to be economically feasible. Cycling experiments should be conducted using realistic desorption conditions and the most realistic flue gas mixture possible with the given instrumentation, with a particular emphasis on the O<sub>2</sub> and H<sub>2</sub>O content of the stream. When available, automated cycling systems with residual gas analysis are ideal for this purpose, as the CO<sub>2</sub> purity and recovery can be extracted directly from the data. Alternatively, rapid cycling can be performed under realistic conditions using a TGA. Post-cycling analysis of the material can then provide insight into the mechanisms of any thermal, oxidative, or hydrolytic degradation.

### Kinetics of adsorption

The low partial pressure of CO<sub>2</sub> in natural gas flue emissions may result in kinetic barriers to effective adsorption/desorption cycling.<sup>44,66,165,166</sup> Therefore, characterization of adsorption and desorption kinetics is needed to assess the viability of new adsorbents and inform the selection of cycle times and bed sizes in a capture process. From a process standpoint, the ultimate kinetics of interest will need to be measured using structured materials, for which kinetics behavior can deviate from the as-synthesized adsorbents. However, at the laboratory scale, thermogravimetric analysis, zero-length column measurements, or breakthrough experiments can be used to assess the rate of CO<sub>2</sub> capture from low partial pressure streams.

### Conclusions

Although natural gas releases half as much CO<sub>2</sub> as coal per kW h energy produced, rapid growth in the consumption of natural gas

and resulting CO<sub>2</sub> emissions necessitates accelerated research into carbon capture from NGCC power plants. Most adsorbents for carbon capture applications are currently at technology readiness levels (TRLs) of 3–5, indicating that few adsorbents have yet advanced beyond laboratory testing to deployment in slipstreams or full-scale power plants.<sup>167</sup> Given that the use of natural gas is increasing rapidly, it is critical that work to bring these materials to TRL 9, which involves deployment in a 500 MW power plant, be given a high research priority. Although a number of prospective materials are under development for CO<sub>2</sub> capture from coal flue gas, air, and crude natural gas, the suitability of these materials for CO<sub>2</sub> capture from NGCC power plants must be established. Here, we have identified the key challenges encountered in the capture of CO<sub>2</sub> from NGCC power plants, as well as some of the most promising materials for this application. We have also proposed a series of characterization methods aimed at guiding adsorbent design and informing process models to assess the viability of new materials for this important process. Overall, more thorough characterization of new materials under realistic conditions is needed in order to advance materials toward deployment in full-scale post-combustion capture processes. Finally, as new capture processes advance toward commercialization, techno-economic and life-cycle analyses should be undertaken to identify optimal cost/benefit opportunities in terms of CO<sub>2</sub> capture rate, total CO<sub>2</sub> emissions avoided, and cost of electricity increase across the power sector as a whole.

## Conflicts of interest

The authors declare the following competing financial interests: J. R. L. has a financial interest in Mosaic Materials, Inc., a start-up company working to commercialize metal-organic frameworks for gas separations, including CO<sub>2</sub> capture applications.

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